SUMMARY

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The Design of a High Pressure Solvent Extraction Process Using Liquid Ammonia as Solvent

The literature on the potential use of liquid ammonia as a solvent for the extraction of aromatic hydrocarbons from mixtures with paraffins, and the application of reflux, has been reviewed. Reference is made to extractors suited to this application.

A pilot scale extraction plant was designed comprising a 5cm. diameter by 125cm. high, 50 stage Rotating Disc Contactor with 2 external settlers. Provision was made for operation with, or without, reflux at a pressure of 10 bar and ambient temperature. The solvent recovery unit consisted of an evaporator, compressor and condenser in a refrigeration cycle.

Two systems were selected for study, Cumene-n-Heptane-Ammonia and Toluene-Methylcyclohexane-Ammonia. Equilibrium data for the first system was determined experimentally in a specially-designed, equilibrium bomb. A technique was developed to withdraw samples under pressure for analysis by chromatography and titration.

The extraction plant was commissioned with a kerosine-water system; detailed operating procedures were developed based on a Hazard and Operability Study. Experimental runs were carried out with both ternary ammonia systems. With the system Toluene-Methylcyclohexane-Ammonia the extraction plant and the solvent recovery facility, operated satisfactorily, and safely, in accordance with the operating procedures. Experimental data gave reasonable agreement with theory. Recommendations are made for further work with plant.

Key Words: Ammonia, Rotating Disc Contactor, Solvent Extraction.

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CONTENTS

1. Introduction

Liquid-liquid extraction is now used extensively in industry particularly in petroleum and petrochemical processing. It is used to refine kerosine, diesel fuels and lubricating oils as well as to separate certain aromatic hydrocarbons from naphthas. The first commercial application of liquid extraction, the Edeleanu Process, was for the preparation of superior quality kerosines using sulphur dioxide as the solvent. The kerosine raffinate produced by this extraction process burned with a brighter and less smokey flame. Later benzene was added to sulphur dioxide to increase the solubility of the hydrocarbons in the solvent. The success of this process encouraged the search for better solvents, improved extractor designs and flexible operating procedures to obtain higher extraction efficiencies.

Liquid ammonia, either in the pure anhydrous form or 'modified' by the addition of anti-solvents or pro-solvents, has been demonstrated on a small scale to be a suitable solvent for extractions ranging from 4-Carbon atom hydrocarbons to the lubricating oil range. Its use might therefore allow a wide variety of feed stocks to be handled by simply modifying the solvent properties. The addition of certain modifying agents does not apparently reduce the selectivity of ammonia. These properties, together with its versatility, suggest that it could have considerable potential as a solvent in future petroleum separation processes.

The tendency is for all but the smallest liquid-liquid extraction processes to be operated continuously. For this reason and economies in operation, e.g. minimum first cost and reduced solvent inventory, the various gravity operated columns find wide application. One common design, the Rotating Disc Contactor, consists of a vertical cylindrical shell divided into a number of separate compartments by a series of stator rings; each compartment contains a disc supported on a centrally driven shaft. The R.D.C. finds extensive use in almost all petroleum extraction processes including deasphalting and naphtha sweetening as well as in the by-product coke, food, metal separation and organic chemical industries. It is simple, easy and cheap to build and offers flexibility in operation, i.e. the ability to vary rotor speed enables a relatively wide range of feed composition or phase ratios to be handled.

In general, however efficient the extractor, the solute concentration in the extract is limited by the phase equilibria. To obtain a more concentrated extract, reflux may be applied in a manner analogous to that in fractional distillation. By this means either the extract purity can be increased or the number of stages required for a specific degree of extraction can be decreased. Reflux is best applied to a Type 2 system since, unlike with a Type 1 system, there is no inherent limitation on the maximum obtainable extract purity. A ternary system

with ammonia as solvent can be converted to a Type 2* system by addition of modifying agents to the solvent, therefore enabling effective application of reflux.

The present work was the first stage of an investigation into the potential of ammonia as a solvent for hydrocarbons separation with, or without,reflux. It involved the determination of equilibrium data for a typical Type 2 system with ammonia as solvent, the design and operation of a pilot scale R.D.C. and ancilliaries for operation at 10 bar pressure, and a preliminary assessment of the advantages and disadvantages of liquid ammonia as a solvent at ambient temperature.

* Type 1 and Type 2 systems are defined in p. 18 – 21

2. Liquid Extraction

2.1. Introduction

Liquid extraction is a mass transfer operation which relies upon differential solubility between the components of a mixture and a third component. It involves the partition of components between two immiscible liquid phases, one of which is added as a solvent. It differs from other separation methods in which an equilibrium distribution is created by addition or withdrawal of heat e.g. distillation, evaporation and crystallisation.

In industry, liquid extraction is most useful where the direct methods either fail or are uneconomic. Typical fields of application are summarized in Table 2.1.

Although liquid-liquid extraction has proved a useful separation method in a number of fields, it has some disadvantages. Since separation is attained by addition of a solvent it is finally necessary to recover the solvent from the product or products. For this duty a solvent recovery system, generally involving distillation or evaporation, must be installed and this introduces additional capital and operating costs. Also, use of the most efficient solvent for the required separation may necessitate expensive materials of construction. However, despite these disadvantages liquid extraction is favoured for many difficult separations.

TABLE 2.1.

FIELDS WHERE LIQUID EXTRACTION IS MOST USEFUL TO APPLY

Separations where Direct Methods are Expensive	Separation of close boiling liquids
	Separation of liquids of low volatility
	Separation of liquids which require high vacuum or flash distillation
	Separation of liquids of high latent heat
	Separation of solids which require high cost fractional crystallisation
Separations where Direct Methods fail	Separation of heat sensitive substances
	Separation of mixtures that form azeotropes
	Separation of components of 'over-lapping' boiling point
Other uses	To replace some expensive chemical methods

Industrial scale application with inorganic processes is limited; however, some important separations such as the separation of rare earths, recovery of cobalt, and nickel purification are achieved by extraction.

Commercially, the petroleum industry is the largest user of liquid-liquid extraction operations. The largest equipment, the highest number of extractors, the greatest variety of extraction processes, and the largest amount of feed material are used in this industry. Nowadays only primary separation of crudes or cracked products is achieved by distillation. Separation of close boiling range fractions by means of chemical reaction utilizing a reagent has been found impracticable. Separation by liquid extraction, in which the solvent dissolves various compounds without chemical reaction, thus permitting complete solvent recovery, offers distinct advantages. In the petroleum industry liquid extraction has played an important role, mainly in hydrocarbon separation, e.g. involving kerosine, lubricating oils and the lighter naphthas, and in desulphurization of petroleum products.

Aromatic type constituents in lubricating oils and the lighter naphthashave a relatively high viscosity-temperature coefficient and therefore have a greater tendency to form sludge-like, and polymerisation, products which considerably impair the quality of oil. The removal of aromatic type hydrocarbons from kerosine oil renders

it colourless and its paraffinity is increased so that it burns brightly without producing soot. Numerous solvents have been proposed for aromatics extraction, but only a few are used on the basis of cost, selectivity and desirable physical properties. For example, nitrobenzene, a highly selective solvent, is not widely used because of its high toxicity. Chlorex has a good solubility-temperature relationship but is corrosive and is therefore not popular (1). Other solvents such as phenol, furfural, propane, formyl-morpholine (2), ethylene-diamine (3), methylsulfoxide (4), and pyridine oxides (5) have been recommended for aromatics extraction and their selectivity and dissolving power have been compared in the literature (6). However, because of their poor solubility-temperature relationships these solvents are not entirely suitable for hydrocarbon separations in the petroleum industry.

Sulphur dioxide has been used to remove aromatic hydrocarbons and sulphur-bearing compounds from naphthenic hydrocarbons. The Edeleanauprocess,using sulphur dioxide as a solvent, was the first commercial application of extraction in petroleum refining (7, 8). To remove materials having low cetane numbers, and some other undesirable materials (such as unstable acidic, sulphur, organo-metallic and nitrogen compounds) diesel oils, fuel oils, burning oils and cracking stocks are extracted

by furfural (8, 9). Diethylene glycol is an alternative solvent to sulphur dioxide for the recovery of aromatics from naphthas (10). Sulfolane has been proposed for the extraction of catalytic reformates; many advantages resulted from its use in place of polyethylene glycol processes (11).

The use of liquid ammonia as a solvent for aromatics extraction appeared to present a system with greater flexibility than any of the other solvent systems. This flexibility arises since the difference in solubility of the aromatic or aliphatic materials in ammonia can be controlled by the addition of antisolvents and prosolvents. Also, since it is non-corrosive, the materials of construction can be of low cost. Two basic disadvantages of using anhydrous ammonia as solvent are its toxicity and relatively high vapour pressure. A comparison of ammonia with other solvents for aromatics extraction is given in Section 2.3.2. and the properties as a solvent are presented in Section 3.

In liquid-liquid extraction, mass transfer is achieved by bringing two unequilibriated immiscible liquids into direct contact then allowing time for equilibrium to be approached by diffusion of one or more solutes across the interface. This results in partial separation of solute from the feed solution. The rate of mass transfer

is expressed by the basic rate equation as follows,

$$N = K A \Delta c \qquad (2.1)$$

where the symbols are as defined in the Nomenclature.

It is clear that high mass transfer rates can be obtained by maintaining the mass transfer coefficient, K, interfacial area, A, and the driving force, Δc at their highest practicable values. A large interfacial area can be created by dispersing one of the phases as droplets in the other. The practical criterion is the interfacial area per unit volume, i.e. the number and size of the droplets in unit volume of dispersion. Therefore, for a high interfacial area appropriate means must be incorporated in extractors to promote dispersion and redispersion. The mass transfer coefficient depends upon the resistances to diffusion within the dispersed and continuous phases. By creating turbulent conditions eddy diffusion, which is more effective than molecular diffusion, occurs; this results in higher mass transfer coefficients. Depending upon the degree of turbulance a wide distribution of droplet size exists in practical contactors. The flow pattern inside and outside the drops, which depends upon the drop hydrodynamics, exhibits 'stagnant', 'circulating' or 'oscillating' behaviour. This is dependent on the Reynolds number within the drops. Stagnant behaviour generally applies only to small drops. Drops larger than about 2mm. diameter, for which $Re < 1$.

exhibit laminar circulation; when Re > 1. turbulent circulation occurs. In general all drops with Reynolds numbers above 200 tend to oscillate. Each flow pattern results in different values for the film coefficient.

In practical extractors mass transfer to or from drops occurs throughout the different stages of drop life. These stages are;

(i) Formation of drops either at a distributor or by agitation

(ii) Release of drops.

(iii) Travel of formed drops throughout the continuous phase.

(iv) Coalescence of drops at a phase boundary e.g. in a settler.

In agitated contactors during travel of the formed drops, mass transfer is complicated by coalescence-redispersion phenomenon which results in a loss of drop identity.

Mass transfer taking place during each of these stages has been studied and correlated by means of mathematical expressions. Recent workers have shown that in a spray column about 10% of the extraction occurs during drop formation, although Sherwood (12) found it was as high as 40% and West (13) observed 14%. It has proved difficult to obtain a precise expression because of rapid changes of dropsize taking place during drop formation. In all expressions the drop is assumed to grow

as a sphere and the coefficient is based on the time of formation and the surface area at the point of detachment. Licht and Conway (14) reported that mass transfer during drop release is of the same magnitude as that during the period of formation. Heertjes and de Nie (15) found that the coefficient was six times greater than the value for the preceding period. However, further work is necessary to obtain a meaningful correlation of mass transfer during drop release.

Mass transfer to or from the formed drops is generally characterised separately for rigid and non-rigid drops. The coefficients for mass transfer in the dispersed phase and in the continuous phase for rigid and non-rigid drops have been expressed in a number of correlations. Details of the correlations, and the range of operating parameters to which they may be applied are described in Section 4.

The expressions derived for the coefficient in the dispersed phase for rigid drops whilst non-stationary diffusion is occurring hold only for small drops. Non-rigid drops can be either circulating or oscillating; in either case mixing in the drop may be by laminar or turbulent circulation depending on the Reynolds number. Complete mixing in the drop occurs by strong oscillations.

A reliable estimate of the transfer coefficient in the continuous phase for a rigid drop is difficult to

obtain because of the contribution made to mass transfer by the wake behind the drop. Therefore, the process has been described as an overall process over the whole drop and a partial coefficient of mass transfer is used. The coefficient is correlated to the variables of the process via the Sherwood number as described in Section 4.

The most reliable correlation for the continuous phase coefficient for oscillating drops is the one by Garner, Foord and Tayeban (16). The mass transfer is again characterised by the Sherwood number.

The contribution to mass transfer during coalescence of drops has not yet been presented in a way enabling it to be taken into account. Coalescence of drops in swarms causes an increase in oscillations and a decrease in surface area. These two factors counteract each other with respect to mass transfer. Prior to coalescence of a drop at an interface, oscillations occur; these are followed by drainage of the film of continuous phase between the drops and the interface. After coalescence the magnitude of the driving force changes over the surface depending on the mechanism occurring.

The overall mass transfer coefficient is found from the dispersed phase coefficient k_d, and the continuous phase coefficient k_c, neglecting the interfacial resistance,

$$\frac{1}{K} = \frac{1}{k_d} + \frac{m}{k_c} \qquad (2.2)$$

The above summary emphasises the importance of droplet behaviour in mass transfer. The equipment should preferably form a monodispersion of drops which oscillate since oscillating drops have the most favourable transfer characteristics.

Another aspect which should be considered for a reliable calculation of extractor efficiency is backmixing. Backmixing has an unfavourable influence on the extraction efficiency because it results in a reduction in Δc. Hydrodynamics and backmixing characteristics are discussed in more detail in Section 4.

The type of extractor to be used is mainly governed by the system properties. In a limited number of cases, a single stage mixer-settler unit may be sufficient, but generally the equivalent of a large number of stages is required.

The contacting devices used in industrial processes are of two types as listed in Table 2.2. These are;

1. Discrete stage contactors, and,
2. Continuous differential contactors in which there is no intermediate separation of phases.

Discrete stage contactors include the mixer-settler range of equipment in which the immiscible liquids are brought into contact and mixed to form a homogeneous

Type of Agitation	Discrete stage contact	Continuous contact
None		Spray column Baffle plate column Packed column Sieve-tray column
Rotary Devices	Holley-Mott Simple mixer-settler Pump-mix mixer settler Individual stage centrifuges Stacked-stage mixer settler	Scheibel column Oldshue-Rushton column Rotating disc contactor Multistage mixer column Polbielniak centrifugal extractor Alfa-Laval centrifugal extractor Luwesta
Pulsed	Pulsed mixer-settler	Pulsed packed column Pulsed sieve-plate column

Table 2.2.

CLASSIFICATION OF CONTACTING EQUIPMENT

dispersion in each stage which is subsequently separated in a gravity operated settler. If the operation is batchwise the same vessel serves for both mixing and settling. Continuous operation is more common with settling taking place in a separate vessel of sufficient size to allow residence time for gravity settling and coalescence. In continuous differential contactors, counter-current flow is promoted by the density difference between the fluids being contacted. The maximum attainable combination of phase flow rates is limited by the flooding rate, above which either of the phases is rejected near its inlet. In some contactors the dispersion can be created simply by passage of the dispersed phase through a distributor, as in a spray column.

Of the range of extractors listed in Table 2.2. the rotary agitated columns, namely the York-Sheibel column, the Oldshue-Rushton column and the Rotating Disc Contactor are finding increased application because of the compromise they offer between cost and operating flexibility. The advantages of most common extractors are compared in Table 2.3.

The RDC has been thoroughly tested in commercial use and found to be highly efficient, simple, cheap to operate and easy to maintain. It is of straightforward construction and has a relatively high volumetric capacity.

TABLE 2.3.

ADVANTAGES AND DISADVANTAGES OF VARIOUS CONTACTORS

Type	Capital Cost	Operating & maintenance costs	Efficiency	Total capacity	Flexibility	Volumetric efficiency	Space		Ability to handle systems that emulsify
							Vertical	Floor	
Spray tower	5	5	1	2	2	1	0	5	3
Baffle plate tower	4	5	2	4	2	3	1	5	3
Packed tower	4	5	2	2	2	2	1	5	3
R.D.C.	3	4	4	3	5	4	3	5	3
Pulsed plate column	3	3	4	3	4	4	3	5	1
Mixer-settler	2	2	3	4	3	3	5	1	0
Centrifugal	1	2	5	3	5	5	5	5	5

Classification 0 - 5 in terms of increasing advantage

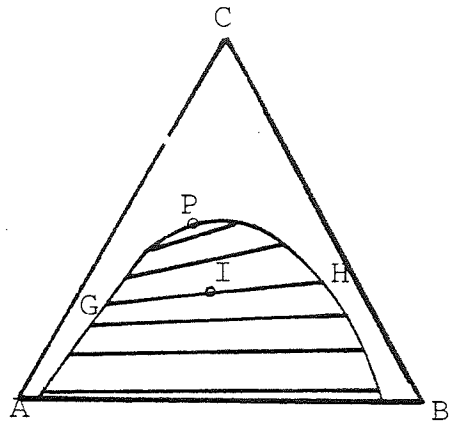
One of its important advantages is that by correct adjustment of geometry and operating parameters there is only limited loss in efficiency on scaling up to larger diameters. It is also possible to operate a column over a wide range of capacities, but retaining efficiency. Applications of the RDC in industry, and design and hydrodynamic characteristics, are given in Section 4.

2.2. The Extraction Process

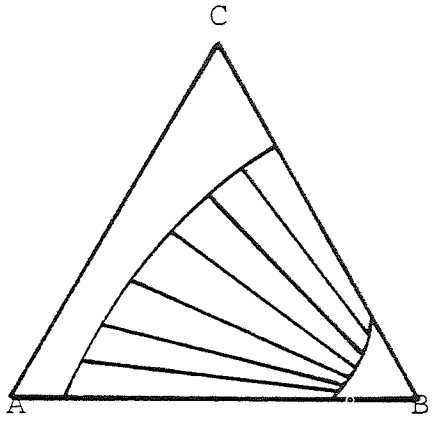
In liquid-liquid extraction studies equilibrium data for three component systems are generally represented on triangular coordinates. Each coordinate represents the composition in terms of each component, solute, carrier liquid and solvent. Any point on or within the triangle represents a mixture of known composition.

Ternary systems in liquid extraction are classified according to the immiscibility between the components. The type of equilibrium curve representing the compositions of the saturated liquid phases at equilibrium at a constant temperature is different for each system. Each triangle in Figure 2.1. illustrates a ternary system. Type 1 and Type 2 systems are of particular relevance to liquid-liquid extraction.

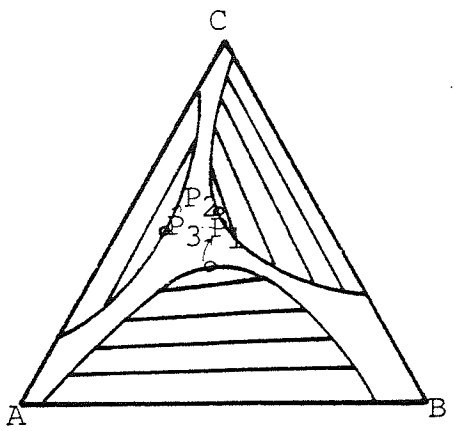
The Type 1 system is the most common; in this system there is one partially immiscible pair, and two



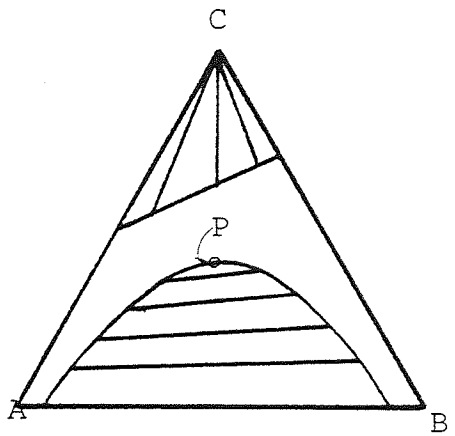
a) TYPE 1



b) TYPE 2



c) TYPE 3



d) TYPE 4

Figure 2.1.

CLASSIFICATION OF LIQUID EXTRACTION PROCESSES

completely miscible pairs. The solubility curve for this type is shown in Figure 2.1.(a). The solute C is completely miscible in solvent B and the carrier liquid A whereas A and B are partially miscible in each other. Any mixture represented by a point below the solubility curve will form two immiscible phases which have compositions at the ends of the tie line passing through that point. In Figure 2.1.(a) the point I represents a composition which will produce two phases of compositions G and H. GH is the tie line through I. An infinite number of tie lines can be drawn in the area beneath the equilibrium curve; these lines are not parallel and usually have changing slopes. At the plait point, P, where the critical condition forms, there is only one phase. Since the solubility of solute C in A and B varies as the temperature changes the shape of the curve is temperature dependent. In some cases there is no critical solution temperature and the isotherms of the equilibrium curve are as shown in Figure 2.2. However, for systems with a ternary critical solution temperature the projected isotherms are as in Figure 2.3.

In the case of Type 2 systems there are two pairs of partially miscible liquids in the ternary system. As shown in Figure 2.1. solute C and raffinate A are completely miscible whereas solvent B is partially miscible

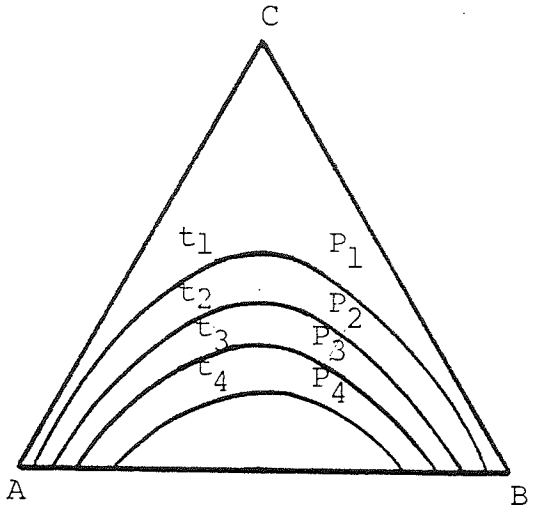


Figure 2.2.

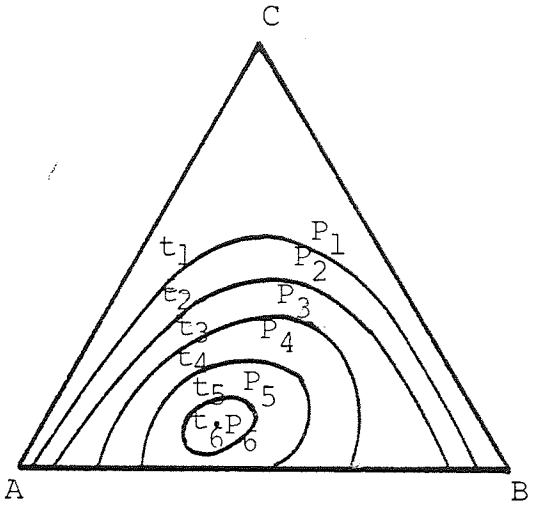


Figure 2.3.

TYPE 1. SYSTEM WITH AND WITHOUT C.S.T.

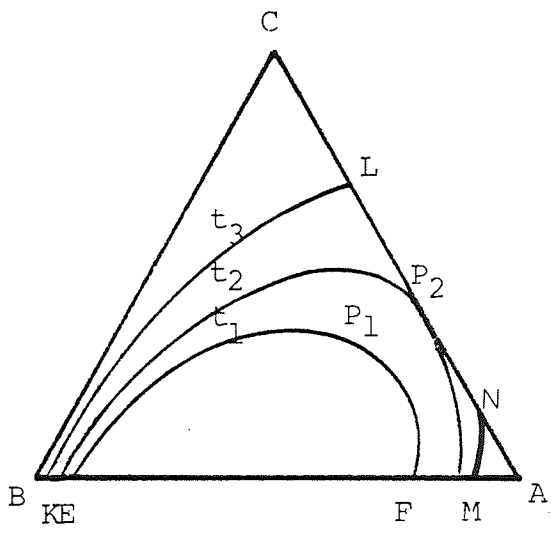


Figure 2.4.

CONVERSION OF TYPE 1. SYSTEM TO TYPE 2.

Curve EP_1F represents a Type 1. System.

Curves KL, MN represent a Type 2. System

in both A and C. The area within the curves represents mixtures that form two phases each at either end of the tie line through the point denoting a specific mixture. Unlike with a Type 1 system there is no plait point. A ternary system exhibiting a solubility curve typical of a Type 1 system at one temperature can change to a Type 2 system at another lower temperature. For example, by reference to Figure 2.4., at t_3 there are two pairs of partially miscible liquids whereas at t_1 there is only one. Hence the system is converted to one characteristic of Type 2 by reducing the temperature from t_1 to t_3. In some cases more complicated temperature changes occur (17). It is often preferable in practice to operate with a Type 2 system rather than a Type 1 system. With Type 1 systems smaller solvent to feed ratios are used than in Type 2 systems. However, in Type 2 systems a better extraction can be achieved with the use of reflux without employing high solvent to feed ratios. The advantages of using reflux are presented in Section 2.2.1. A Type 1 system may also be converted to a Type 2 system by the addition of an anti-solvent. For example, with the ternary system Toluene-Methylcyclohexane and anhydrous liquid Ammonia a Type 1 system is converted into a Type 2 system by addition of water as an anti-solvent to Ammonia.

In a Type 3 system all three pairs of components in the ternary system are partially miscible with one another. This phenomena occurs very rarely. Normal

extraction processes are not able to separate systems of this type.

Type 4 systems are those which involve the formation of a solid phase. Only a few of this type such as the ternary systems aniline-iso-octane-naphthalene or methyl-ethyl-ketone-water-calcium carbonate are of importance for liquid extraction.

Separation of the components of a mixture by application of liquid-liquid extraction can be brought about in a variety of ways. The techniques used industrially can be classified depending upon the type of solvent system and the physical arrangement of the equipment. This is demonstrated in Table 2.4.

Table 2.4. CLASSIFICATION OF INDUSTRIAL EXTRACTION TECHNIQUES

<table>
<tr><td rowspan="3">Solvent System</td><td colspan="3">Single Solvent</td></tr>
<tr><td colspan="3">Mixed Solvents</td></tr>
<tr><td colspan="3">Double Solvents</td></tr>
<tr><td rowspan="5">Physical Arrangement of Equipment</td><td rowspan="5">Stagewise</td><td colspan="2">Single Contact</td></tr>
<tr><td colspan="2">Differential Contact</td></tr>
<tr><td rowspan="3">Multiple Contact</td><td>Co-Current</td></tr>
<tr><td>Counter-Current</td></tr>
<tr><td>Counter-Current with Reflux</td></tr>
</table>

Operations with most ternary systems use a single solvent system, i.e. separation is achieved at a convenient temperature and pressure by using only one solvent. In some cases a satisfactory separation can be achieved using a mixed solvent system comprising a solvent solution of at least two components, one of which is added either to increase or to decrease the solubility. Some processes use double solvent systems in which solutes are distributed between two immiscible or partially miscible solvents. In the Duosol process, which is the outstanding example of the commercial application of double solvents, a mixture of phenol and cresylic acid is used as the selective solvent and propane as the non-selective solvent. The propane acts both as a diluent to reduce the viscosity of the lubricating oils being extracted and as a precipitant of the asphaltic constituents.

As described earlier,there are two types of equipment based on stagewise or continuous contact. Stagewise contact can be accomplished in a number of ways depending on the arrangement of the stages as shown in Table 2.4. For continuous stagewise contact, usually in a vertical baffled tower or a mixer-settler cascade, design calculations are generally based on a height equivalent to a theoretical stage or a stage efficiency.

Differential contact is analogous to differential distillation and involves extraction of a definite amount

of solution by differential portions of solvent. Extracts formed are removed in differential portions.

Multiple contact can be cross current or countercurrent, but the latter is almost always preferred since it gives optimum use of solvent.

Countercurrent contact involves a number of stages arranged together to form a cascade. Feed and solvent enter at the opposite ends of the cascade. Extract and raffinate flow countercurrently in each stage. Countercurrent contact with reflux is analogous to fractional distillation. The reflux is formed by returning a portion of the extract from which solvent has been removed. Since the ultimate aim in this project is the application of reflux, this technique is reviewed in detail.

2.2.1. Counter Current Extraction with Reflux

The use of reflux in liquid-liquid extraction was first introduced in the 1930's, but it is not commonly used industrially. It is usually applied to homologous systems where the distribution coefficient and separation factor are low.

Extraction with reflux is analogous to complete rectification in distillation. As in fractional distillation, reflux is most useful if high purity extract is required, or when the number of theoretical stages

required for a desired separation would otherwise be exceedingly high. In countercurrent extraction processes it is theoretically possible to obtain a pure raffinate with an infinite tower height or infinite number of stages since under this condition the raffinate leaves the extractor in equilibrium with the fresh solvent entering. However, the final raffinate phase composition depends on the sign of the slope of the tie line through point I in Figure 2.6. (a), (b). Thus for the ternary system shown in (a), the raffinate can be obtained in any desired purity whereas in (b) the maximum purity of the raffinate is limited by the point K. In general, nothing can be done to overcome this limiting factor if the slopes of the tie lines cannot be changed with changing temperature. The extract product purity is limited since the extract leaves the extractor in contact with the feed entering as demonstrated in Figure 2.5. In order to enrich the extract purity beyond the point where it is in equilibrium with the feed, reflux could be employed. This reflux is supplied by returning a portion of the extract from which solvent has been removed. Systems using reflux require the feed to enter at an intermediate point in the column as shown in Figure 2.5. The final extract will now be in equilibrium with the raffinate stream leaving stage (1) which is reduced in solvent content in the solvent recovery unit. This results in a sharper separation.

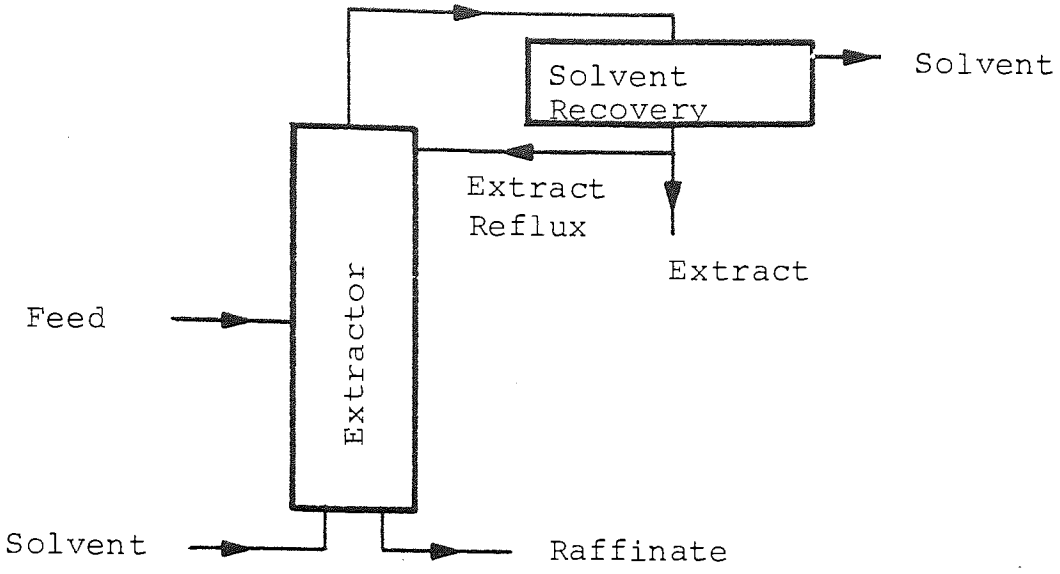


Figure 2.5

COUNTERCURRENT EXTRACTION WITH REFLUX

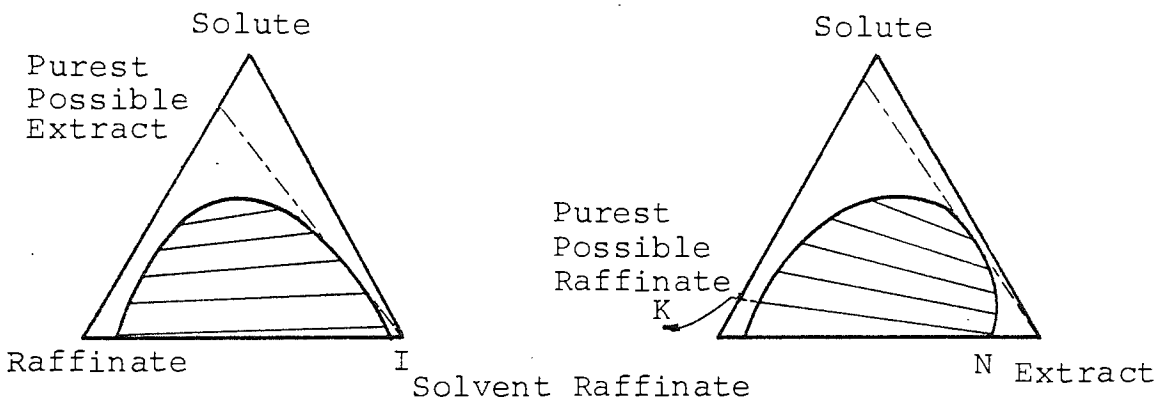


Figure 2.6.

TYPE 1 SYSTEM

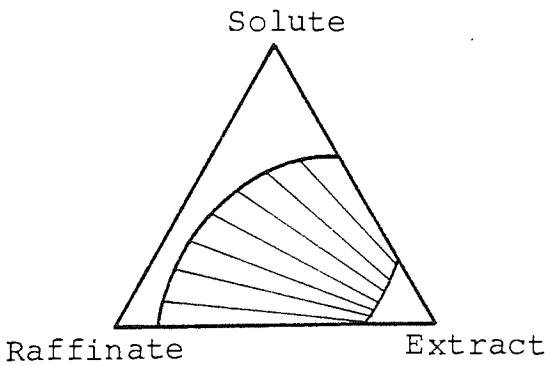


Figure 2.7.

TYPE 2 SYSTEM

A sharp separation can alternatively be attained at the expense of more solvent per unit mass of feed, but this may be impracticable since more energy, and a larger plant, will be required for solvent recovery.

Although the advantages of using reflux in liquid extraction are evident, it is essential to first consider the nature of the ternary system.

Unlike distillation, the use of reflux in extraction is subject to some limitations. With a Type 1 system, in which the solute is completely miscible in the solvent and the carrier liquid is partially miscible in the solvent, whether or not reflux is applied, the purity of the extract product is limited by the tangent from the solvent point to the saturation curve as shown in Figure 2.6. (a) and (b). With a Type 2 system there is no such limitation on the purity of the extract obtained. However, in both Type 1 and Type 2 systems raffinate can be provided in any desired purity if the slope of the tie lines are of the right sign.

It has been experimentally confirmed that, although extract reflux was essential to obtain an extract product of high purity, raffinate reflux has no appreciable effect on the efficiency of operation (18). Furthermore, it has been shown by calculation that the

number of theoretical stages required for a given separation is unaffected by the use of raffinate reflux (19, 20).

By analogy with distillation, extract reflux can be applied either to obtain a pure extract or to reduce the number of stages. On this basis extract reflux might be beneficial even for a Type 1 system, but the economic advantages can only be estimated for each case individually.

Methods to Provide Extract Reflux

Extract reflux can be provided in a number of ways. The usual method is to recover solvent from the extract leaving the contactor, by distillation or evaporation, and to return it to the column. This is termed "external reflux". Alternatively reflux may be provided by the withdrawal of heat from the extract phase or by the addition of an antisolvent to the system. These two methods are known as "internal reflux".

If the system is Type 1 and it is desired to form reflux by withdrawal of heat in order to obtain a raffinate and an extract of high purity, it should first be converted to a Type 2 system. This removes limitations on the concentration of the extract. The effect of temperature on the shape of the solubility

curve has been discussed in Section 2.1. Thus, under certain conditions a Type 1 system can be changed to a Type 2 system by reduction in temperature. In theory, extraction can be carried out at a temperature which would produce an optimum-shaped solubility curve. However, this method is not always applicable since to obtain an equilibrium curve of Type 2 with some ternary systems would require the temperature to be lowered to a value below which one of the components solidifies. Also at low temperatures other factors which directly affect operation, such as mass transfer rate and distribution coefficients, are depressed so that it would be necessary to use a large number of stages and a large solvent to feed ratio .

In practice, in extraction processes using this procedure, solvent and feed are introduced into the extractor at different temperatures thereby promoting a temperature gradient along the column (21).

Formation of reflux by the addition of an anti-solvent involves a similar route to that produced by reduction in temperature. An antisolvent, which is partially or completely miscible in the extracting solvent, is added to reduce the solubility of the solute in the solvent. In this way a Type 1 system can be converted to a Type 2 system. In a countercurrent extraction

process in which solvent and feed are introduced at opposite ends of the extractor unit, the antisolvent is fed in near the extract outlet. Only a relatively small amount of antisolvent is required. However, formation of reflux by the addition of an antisolvent often has the disadvantages of introducing a low mass transfer rate and also low distribution coefficient. Therefore, the method is not always practicable.

2.2.2. Methods of Calculation

In a Type 2 system, reflux can be applied by the return of a portion of the extract from which solvent has been removed. A flowsheet of a stagewise countercurrent extraction operation involving reflux is given in Figure 2.8.

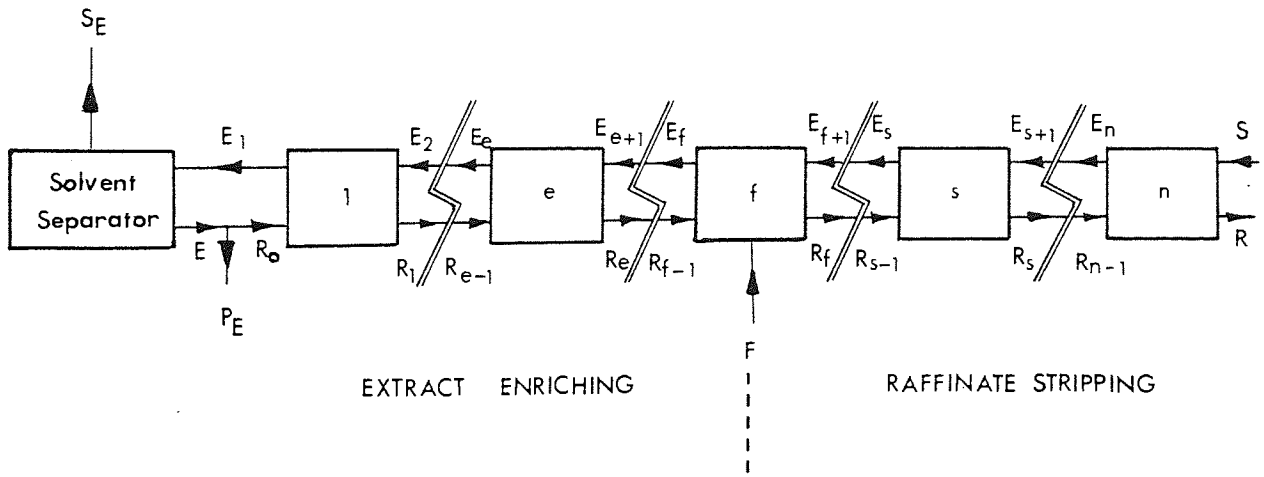


Figure 2.8.

COUNTERCURRENT EXTRACTION WITH REFLUX

Feed is introduced to stage (f), the middle of the extraction unit. In stages (f-1) to (1) the solute content of the extract is increased; this comprises the extract enriching section. The final extract leaving stage (1) passes to a solvent recovery unit to produce a solution E' with a reduced solvent content. Part of this constitutes the extract product and the remainder is returned to stage (1) as reflux. The solvent recovery unit should remove sufficient solvent to ensure that E_1 and E' are on opposite sides of the equilibrium curve. In stages (f+1) to (n) the solute content of the raffinate is reduced. The raffinate leaves stage n and, as explained earlier, no advantage would be obtained by employing reflux at the raffinate end. A typical operating diagram is given in Figure 2.9. The method of calculation based on triangular coordinates is an extension of that used for countercurrent extraction without reflux. There is a constant net flow in one direction in each section of the extractor. At the extraction end the net flow is E_1-R_o and its composition is represented as Q on the straight line drawn through R_o and E_1. Its location is such that,

$$\frac{\overline{R_oQ}}{\overline{E_1Q}} = \frac{\text{Amount of Extract Phase } E_1}{\text{Amount of Reflux } R_o} \qquad (2.3)$$

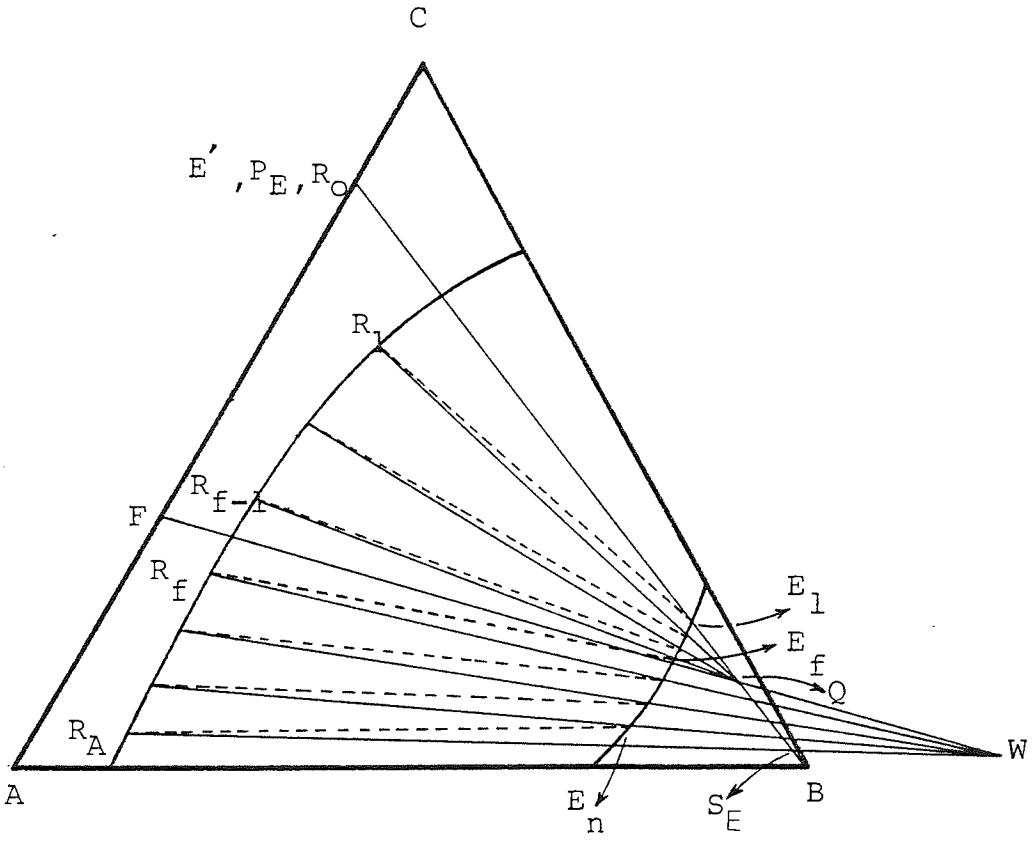


Figure 2.9.

COUNTERCURRENT EXTRACTION WITH REFLUX

The point Q is the operating point for the enriching section. In the stripping section the net flow is changed by the addition of the feed F to the column. The net flow for this section is represented by point W in the line drawn between Q and the feed F. This point is on the line drawn between the solvent point and the final raffinate phase as shown in Figure 2.9.

The reflux ratio $(\frac{R_o}{P_E})$ can be determined in terms of the composition of any one of the three components with the aid of a mass balance and ternary equilibria on the triangular coordinates.

$$\frac{R_o}{P_E} = \left(\frac{\overline{E_1 Q}}{\overline{P_E E_1}}\right)\left(\frac{\overline{P_E S_E}}{\overline{Q S_E}}\right) \qquad (2.4)$$

This can be expressed in terms of compositions,

$$\frac{R_o}{P_E} = \frac{(X_{A_{E_1}} - X_{A_Q})(X_{A_{P_E}} - X_{A_{S_E}})}{(X_{A_{P_E}} - X_{A_{E_1}})(X_{A_{S_E}} - X_{A_Q})} \qquad (2.5)$$

The internal reflux ratio in the stripping section is given by,

$$\frac{R_{s-1}}{E_s} = \frac{\overline{E_s W}}{\overline{R_{s-1} W}} \qquad (2.6)$$

Equation (2.6) applies to stages (f+1) to (n) but the ratio varies for each stage.

Minimum Reflux Ratio

One of the limiting conditions in reflux application is the minimum reflux ratio with an infinite number of stages. At minimum reflux ratio a pinch condition exists where a tie line lies parallel to an operating line and further extraction cannot take place. This condition occurs when the extension of any tie line passes through the operating points Q or W. From Equation (2.4), the nearer the intersection of the tie line with $\overline{R_O E_1}$ lies to point Q the greater is the reflux ratio and hence the smaller the number of stages required. The minimum reflux ratio condition is shown in Figure 2.10 (a).

Total Reflux

With increasing reflux ratio the solvent to feed ratio increases and the number of stages required for a given separation decreases. In the limit, the products P_E and R_n and the feed F have infinite values compared with R_O and S, and this corresponds to total reflux operation. At total reflux, the points Q and W coincide with S on the diagram and the number of stages required is minimum. A countercurrent extraction arrangement operating at total reflux is shown in Figure 2.10 (b).

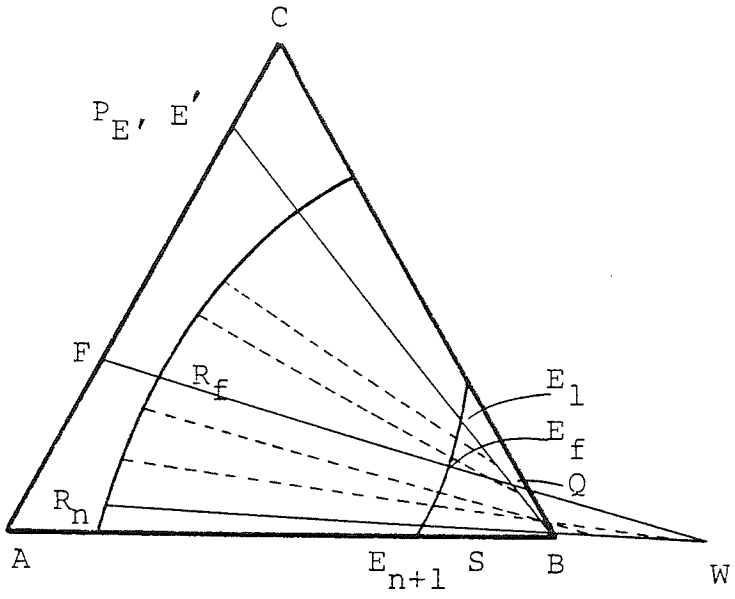


Figure 2.10(a)

DETERMINATION OF MINIMUM REFLUX RATIO

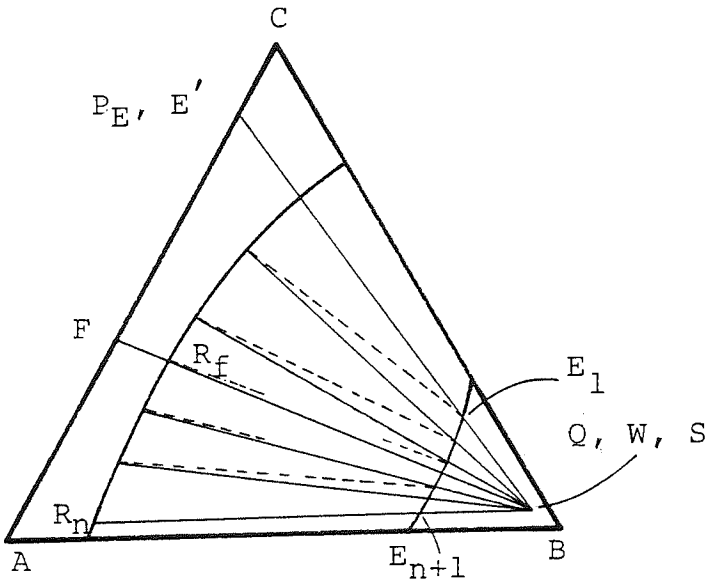


Figure 2.10(b)

MINIMUM NUMBER OF STAGES AND TOTAL REFLUX

Ideally, a plant should be operated at the optimum reflux ratio determined from an economic balance including the cost of stages and, the cost of solvent recovery. The total cost,which is the sum of the operating and fixed costs, shows a minimum and this coincides with the optimum reflux ratio.

Rectangular Coordinates

Determination of the number of equilibrium stages for a given separation using triangular graphical construction is sometimes difficult because at the low concentration of components in the solvent or extract phase the operating lines are close together. The alternative of arithmetical stage to stage calculations on a solvent or solvent-free basis is tedious and time consuming. Rectangular graphical construction permits simple and rapid determinations.

Distribution and Janecke coordinates are used for this purpose. Janecke coordinates are most useful for calculating the number of stages in liquid extraction operations with reflux since variation of reflux throughout the column is clearly shown. Good accuracy is obtained by expressing the composition changes on a solvent-free basis in mass or volume ratios.

Mathematical Methods of Calculation

Calculation of extraction operations are usually

done to determine one of three main requirements i.e. the number of theoretical stages, the reflux ratio, and solvent to feed ratio.

As already outlined these can be determined by graphical methods or by stage to stage calculations. Stage to stage calculations are usually tedious and tend not to be used. For the calculation of complex mixtures extraction when complete phase equilibrium data are not available a third method, developed by Fenske and Varterressian (22, 114), is used. It is applied if only the selectivity is known and is constant.

Selectivity, discussed later in section 2.3. is defined by,

$$\beta_{CA} = \left(\frac{X_{CB}}{X_{AB}}\right) \Big/ \left(\frac{X_{CA}}{X_{AA}}\right) \qquad (2.7)$$

i.e. the ratio of C to A in the solvent rich phase divided by the ratio of C to A in the solvent lean phase. At total reflux, when F is constant, the minimum number of stages in the enriching section is;

$$\left(\frac{X_C}{X_A}\right)_E = \beta^{ne} \left(\frac{X_C}{X_A}\right)_F \qquad (2.8)$$

In the stripping section the number of stages is;

$$\left(\frac{X_C}{X_A}\right)_F = \beta^{ns} \left(\frac{X_C}{X_A}\right)_R \qquad (2.9)$$

Ratios $\left(\frac{X_C}{X_A}\right)$ with subscripts E, F and R are the ratios of C to A in the extract, feed and raffinate respectively. The total minimum number of stages is;

$$\left(\frac{X_C}{X_A}\right)_E = \beta^{n} \left(\frac{X_C}{X_A}\right)_R \qquad (2.10)$$

and the minimum reflux ratio is given by,

$$\left(\frac{R_o}{P_E}\right)_{min.} = \frac{1}{\beta-1} \left[\frac{(X_C)_E}{(X_C)_F} - \beta \frac{(X_A)_E}{(X_A)_F} \right] \qquad (2.11)$$

The solvent to feed ratio is related to minimum reflux ratio by (35),

$$\left(\frac{S}{F}\right)_{min.} = \left(\frac{R_o}{P_E} + 1\right) \left(\frac{\text{Wt. \% S}}{\text{Wt. \% F}}\right)_{SF} \left(\frac{P_E}{F}\right) \qquad (2.12)$$

where $\frac{R_o}{P_E}$ = reflux ratio; (R_o, P_E in mass units)

$\frac{S}{F}$ = solvent to feed ratio by weight

$\left(\frac{\text{Wt. \% S}}{\text{Wt. \% F}}\right)$ = ratio of Wt. % solvent to feed in solvent phase leaving feed point.

$\frac{P_E}{F}$ = extract to feed ratio by weight.

All the above relationships only hold for the condition of constant selectivity. Alternatively, an

average value for β can be used as an approximation. However, whenever possible graphical methods are applied since they give rapid and accurate results.

2.2.3. Feasibility of Reflux

Although the use of reflux in liquid extraction was known in the 1930's its industrial application has been limited due to lack of data (18). Until the 1950's only one process made use of extract reflux; this was the refining of vegetable oils using furfural as solvent. Lately reflux has been incorporated into aromatics recovery processes. In the Udex process, which uses diethylene glycol as solvent for the removal of aromatics from refined naphthas,reflux has been applied to obtain a pure product (25, 26). Also, in the Sulfolane process, efficient recovery of aromatics makes use of reflux which is produced in a flash separator (27).

Industrial application of liquid extraction with reflux in the petroleum and petrochemical industries is becoming more extensive due to increasing demand for high purity products which are otherwise difficult and uneconomical to obtain. Liquid ammonia has been suggested as a versatile solvent for the separation of aromatics. As the addition of modifying agents does not cause a deterioration in the unique characteristics of ammonia as a solvent, a Type 2 system can be formed by controlling the solubility of ammonia

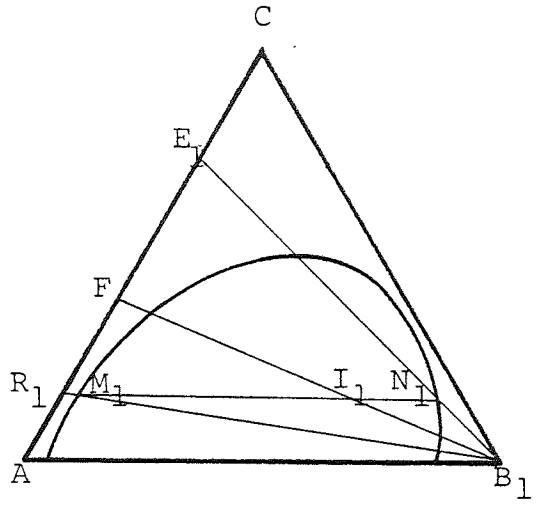
by the proper choice of a modifying agent. This should enable efficient use to be made of reflux.

2.3. Solvent Selection

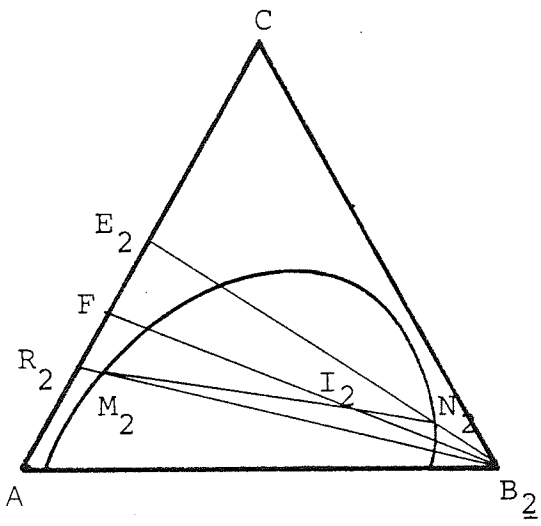
In industrial liquid-liquid extraction processes it is desirable to find a solvent with optimum properties. No single solvent will possess all the desirable properties for a particular system, that is the advantage of one property may be counteracted by the disadvantage of another. Therefore, a compromise has to be made based on the relative importance of the factors that affect the versatility of a solvent. Special consideration must be given to the case of removal of the solvent from the products since this is the most expensive part of the entire separation process. The main factors to be considered in the selection of a solvent and a recovery process are summarised below.

2.3.1. Choice of a Solvent

Selectivity: Selectivity, β, which is analogous to relative volatility in distillation, is the prime concern because it directly affects the separability of solvent. Figure 2.11 (a) illustrates a ternary system in which B_1 is the solvent. Point I_1 is the resultant composition of the mixture obtained upon addition of solvent B_1 to solution F. After equilibrium is achieved, by mixing followed by settling of the two insoluble



a) Separation of C from A by means of solvent B_1.



b) Separation of C from A by means of solvent B_2

Figure 2.11

COMPARISON OF THE SELECTIVITY OF SOLVENTS

phases, M_1 and N_1 would represent the compositions of these two equilibrium layers. Line $\overline{M_1N_1}$ is the tie line connecting two equilibrium compositions through I_1. E_1 and R_1 represent the compositions of the final products from which solvent has been removed, i.e. solution F is separated into two mixtures R_1 and E_1. Obviously it is desirable for the distance between R_1 and E_1 to be a maximum. Use of another solvent B_2, as shown in Figure 2.11 (b) results in compositions R_2 and E_2. Clearly separation is less successful in this case; this is due to the direction of slope of the tie line through I_2.

Solvent B_1 is hence more selective than solvent B_2. The selectivity of solvent B for solute C would then be the ratio of C to A in the solvent-rich phase divided by the ratio in the solvent-lean phase.

$$\left(\frac{X_{CB}}{X_{AB}}\right) = \beta_{CA} \left(\frac{X_{CA}}{X_{AA}}\right) \qquad (2.13)$$

High values for β are desirable in practical liquid extraction processes. If $\beta \rightarrow 1$ a large number of theoretical stages is required for a useful separation. Re-arranging Equation (2.13)

$$\beta_{CA} = \left(\frac{X_{CB}}{X_{CA}}\right) \left(\frac{X_{AA}}{X_{AB}}\right) \qquad (2.14)$$

Equation (2.14) indicates the effect of solubility i.e. the ratio $\frac{X_{AA}}{X_{AB}}$ on selectivity; the lower the solubility of A in B the higher is this ratio and therefore the higher the selectivity. For a few systems the selectivity is substantially constant but generally it varies with solute concentration. The effect of temperature on the selectivity is much smaller than the effect of solubility; therefore if a solvent has insufficient selectivity at one temperature it is unlikely to be selective at another temperature. The effects of temperature and concentration on selectivity of a specific solvent are in general such that the selectivity tends to increase slightly as the temperature falls; and to decrease as the concentration of solute rises at constant temperature.

Distribution Coefficient: the distribution coefficient should be considered together with the selectivity since the latter is directly related to it. Substituting m_c for $\frac{X_{CB}}{X_{CA}}$ in Equation (2.14).

$$\beta_{CA} = m_c \frac{X_{AA}}{X_{AB}} \qquad (2.15)$$

Since $\frac{X_{AA}}{X_{AB}} > 1$, the value of selectivity is dependent on the distribution coefficient. If $m_c > 1$, then it follows that

$\beta > 1$. For systems in which $m_c < 1$, it may also be possible for $\beta < 1$. The distribution coefficient can be adjusted when the extracting solute is an ionizing substance by altering the pH of the solute or by 'salting out' following addition of an unextracted salt.

Capacity: It is not desirable to use a solvent of high selectivity if the quantity of the extracted solute is low. High solvent to feed ratios are required for higher capacities which may be uneconomical. The solvent to feed ratio required for a given separation is of prime importance since the solvent rate controls the dimensions of the extractor, and the energy requirements and size of the recovery plant.

Solubility: The importance of solvent solubility was referred to earlier with regard to selectivity. The carrying power of a solvent is measured by its solubility characteristics. This is an important feature of a solvent since it affects the solvent to feed ratio for a given separation, and the equipment size.

As mentioned earlier the solubility of a solvent may be modified in several ways such as by the imposition of a temperature gradient or by the addition of modifying solvents or antisolvents. The solubility-selectivity relationship is of prime importance in solvent selection. Many solvents have high selectivity and low solubility

and cannot be modified without extensive treatment. An ideal solvent would have a high selectivity and high solubility. However, solvents commonly exhibit a reduction in selectivity with an increase in solubility.

Density: The density of a solvent plays an important role in extractor operation and, in some cases, in the solvent recovery system. Sufficient difference is required between the densities of the extract and raffinate phases for rapid settling and separation to occur either in the extractor or in external settlers. The greater the difference in the densities of the contacted phases the greater the rate of disengagement of the immiscible layers and the greater the volumetric capacity of the contactor. In some ternary systems it is possible for the two immiscible layers to be at the ends of a tie line of the same density. This phenomenon, which results in settling difficulties, may be solved by a change in temperature.

The key properties of selectivity, solubility, capacity and density have been discussed. However, additional factors are relevant to solvent selection, namely some other physical, thermodynamic and chemical properties. A low viscosity is preferable since a high viscosity could result in settling problems by entrainment of fine drops and would increase the pressure drop through the extractor and associated piping.

A high interfacial tension favours rapid coalescence and hence eases separation, but necessitates an increased level of energy for dispersion. Too low an interfacial tension may lead to the formation of a stable emulsion. The freezing point of a solvent becomes important only when storage may be at low ambient temperatures or when a cooling operation is used to recover the solvent, i.e. a low temperature may cause crystallisation in the system. The vapour pressure of a solvent has an important effect on equipment cost. High pressure equipment may be required for volatile solvents whereas a low volatility usually requires a high temperature for solvent recovery. Further, higher solvent losses may be associated with increased volatilities. Heat of vaporisation and specific heat also affect solvent recovery costs. When the solvent is vaporised by an external heat source, such as steam for recovery, a high heat of vaporisation is a disadvantage. Conversely, a high heat of vaporisation together with a reasonable volatility permits a self-refrigeration process to be used for solvent recovery (e.g. as with ammonia). Chemical stability of the solvent is important since any permanent chemical reaction between the solvent and the feed stock is undesirable; only in their absence will the yield of products and recovery of solvent be complete. Loose chemical bonding can enhance the separation, but, unless the bonds can be

broken easily, solvent recovery becomes a problem. The thermal instability of some solvents can complicate the recovery system by formation of gums or polymers or, in some instances, by decomposition into components of lower molecular weight. In any case, a solvent prone to instability imposes a serious economic burden on the process. Corrosivity, toxicity and flammability are other properties which may limit a solvent's usefulness. A solvent should preferably not cause severe corrosion problems with normal materials of construction, but relative economics may favour the use of more expensive materials. Problems associated with toxicity and flammability can also be minimised by properly designed equipment if economics are otherwise favourable. Finally the cost of solvent must be considered for two reasons. Firstly, a large inventory of solvent is likely to be required. Secondly, the expense of make-up for solvent losses over a period of time can become prohibitive.

2.3.2. Accepted Solvents for Aromatics Extraction

The importance of the application of extraction processes to aromatics separation was mentioned in Section 2.1. For optimum process economics the choice of solvent has to be considered together with two other aspects, namely the design of more efficient extractors and the process arrangement. Some of the

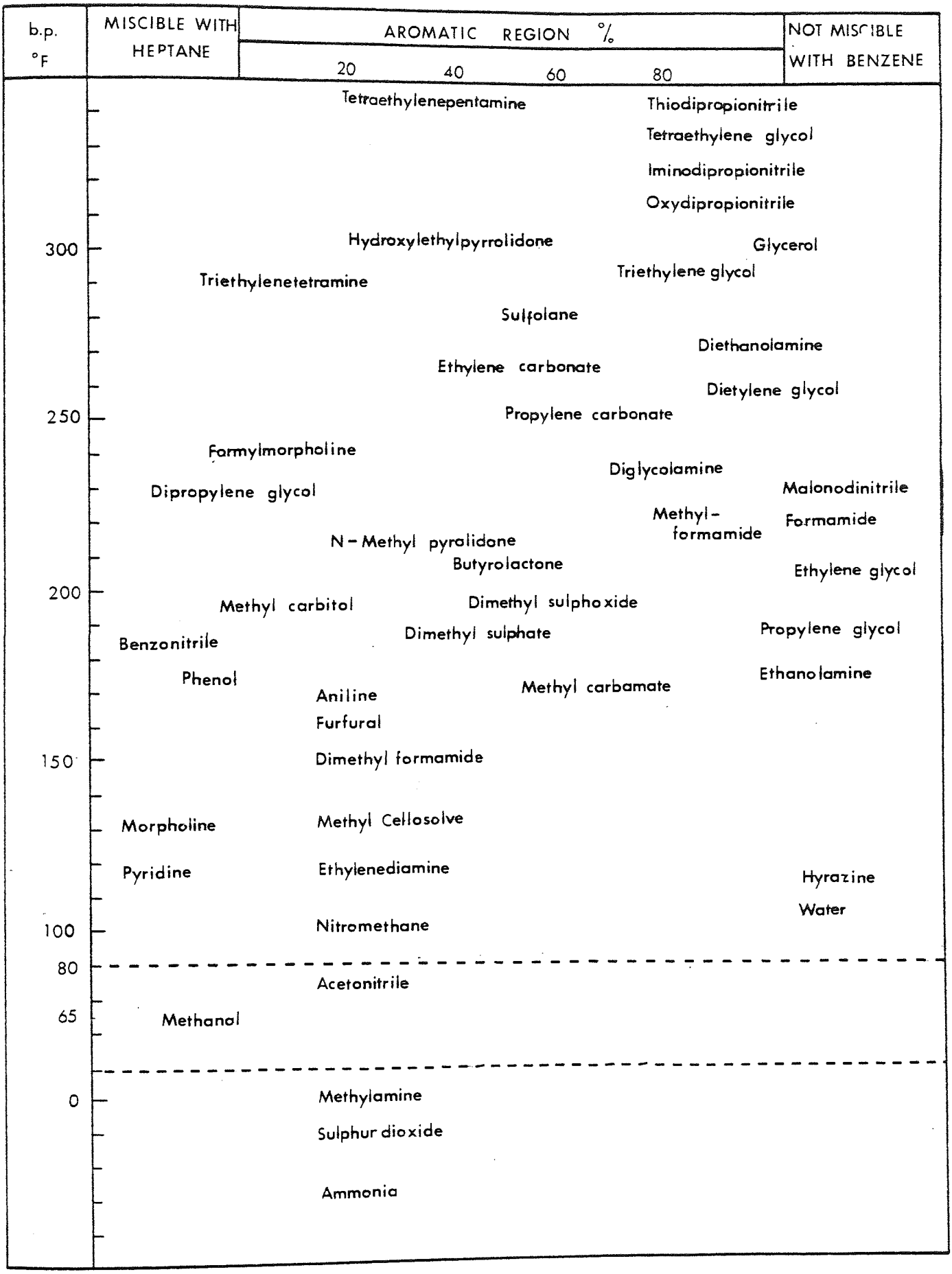
solvents used in the petroleum industry were mentioned in Section 2.1. together with a brief comparison. In Section 3 ammonia is considered as a selective solvent with many favourable properties. Some major characteristics of solvents recommended for aromatics extraction will now be discussed in detail.

Liquid sulphur dioxide was first discovered as a selective solvent for the separation of aromatics from non-aromatic hydrocarbons about 50 years ago. Since then its use has become the basis for one of the major processes in the petrochemical and organic chemical industries. However, about 50 solvents have been discovered which can be seriously considered for aromatics extraction. A considerable amount of experimental work and calculation is necessary to find the optimum solvent since,as described earlier, every change in properties yielding an advantage may also involve a disadvantage in another respect.

The solvents that can be used in the petroleum industry are arranged in Figure 2.12 according to their boiling point and polarity. This diagram shows the miscibility of solvents taking heptane and benzene as criterion. The effect of different polarity of solvents A and B is illustrated in I-IV in Figure 2.13. A low polarity results in diagram IV; this is undesirable since an efficient extraction is impracticable with such a large two phase region.

Figure 2.12

COMMON SELECTIVE SOLVENTS FOR AROMATICS ARRANGED ACCORDING TO BOILING POINT AND POLARITY



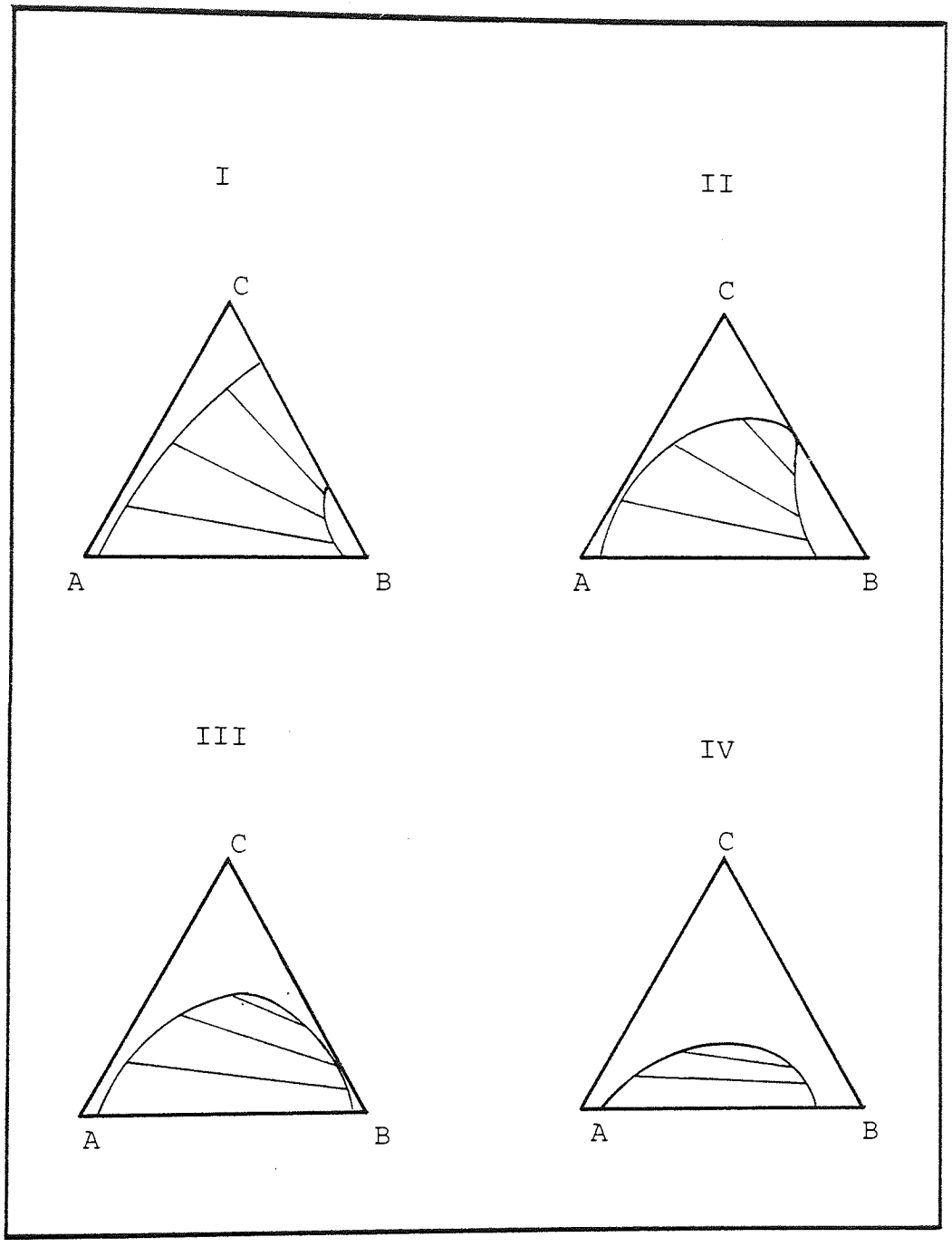


Figure (2.13)

POLARITY OF SOLVENTS DECREASING

FROM I to IV

Solvent b.p. and latent heat are important since separation from the extracted solute is generally by distillation and the cost of this significantly affects the economics of the process.

The major importance of selectivity and capacity have been discussed earlier. Figure 2.14 presents a comparison for the solvents used in the separation of hydrocarbon mixtures. On this diagram an ideal solvent would be located in the right hand top section of the diagram. It is desirable to determine where the economic optimum lies between selectivity and capacity. Most solvents with a high selectivity and a high capacity would fail to meet other criteria.

Although several solvents have a high selectivity for aromatics separation most are unsuitable for other reasons. Some are thermally unstable and any chemical reaction during heating may affect the economics of the process, even if the reaction rate is very low. Some solvents decompose into gaseous constituents like formamide, and subsequently carbon monoxide and ammonia, and are therefore unsuitable. Alternatively, if decomposition of the solvent results in a condensable product, as in the case of propylene carbonate, which decomposes into carbon dioxide and acetone, post purification of the aromatics is required (28). In all cases the

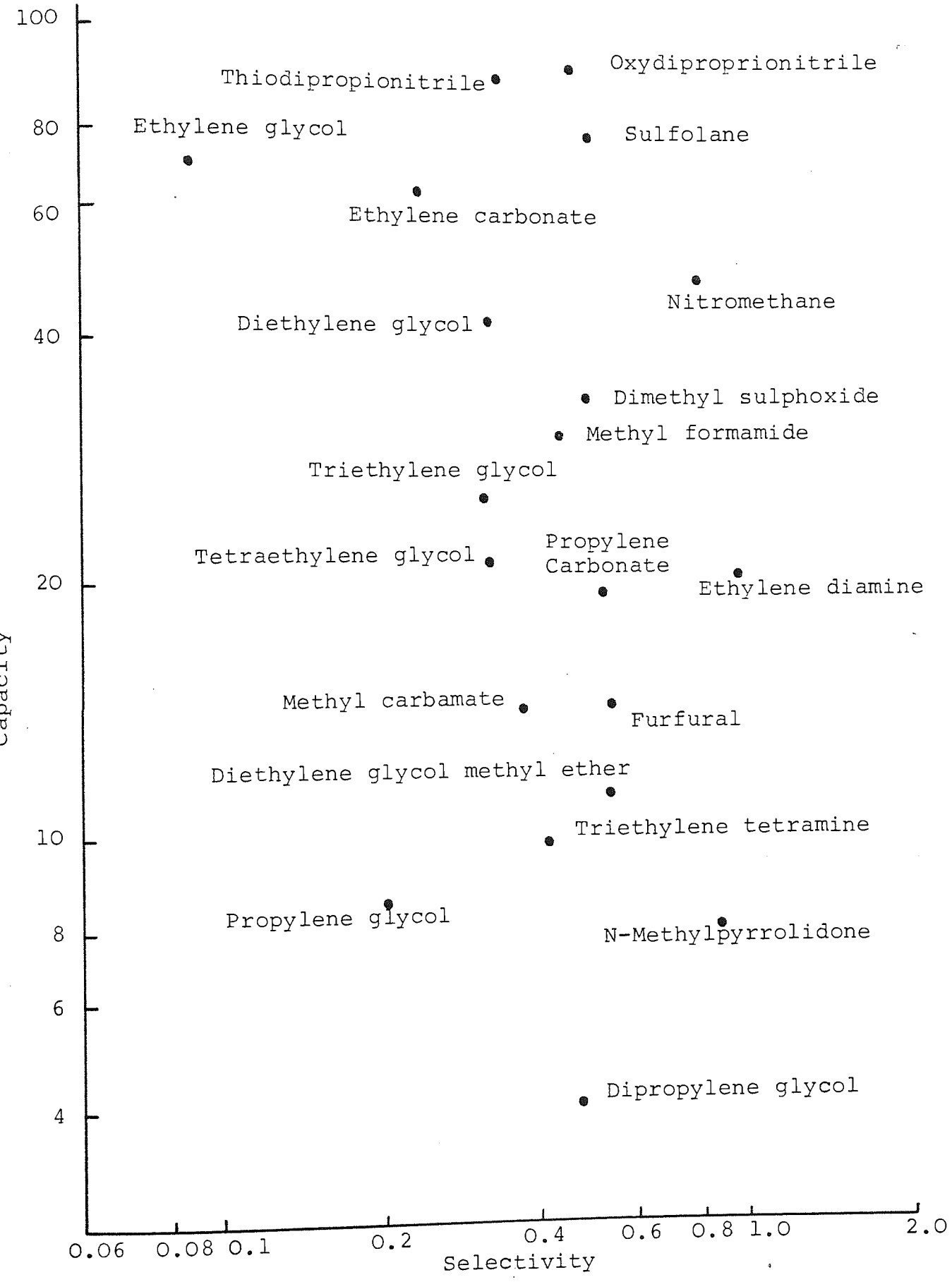


Figure 2.14

CAPACITY AND SELECTIVITY OF SOLVENTS FOR AROMATICS EXTRACTION

solvent loss has to be made up. Furfural, although it is a selective solvent, tends to polymerise, so that a regenerator has to be operated for polymer removal.

The effects of viscosity and density were explained previously and are factors to be considered for an optimum solvent. A high density difference between the two phases will promote phase separation and a low viscosity favours both phase separation and mass transfer.

The versatility of a solvent plays an important part in minimising the capital cost of plant for the extraction of aromatic hydrocarbons. The ability of a solvent to extract over a wide boiling range, by modifying the solvent so that the solubilities of materials in the feed stock are altered, is advantageous. It enables feeds of varying composition to be processed. This feature becomes more advantageous as the extraction becomes more complex in order to treat different crude oils and produce a wider variety of products.

Irrespective of their selectivity, the most commonly employed solvents like diethylene glycol, sulphur dioxide, furfural, phenol and propane are used only for the separation of particular feed stocks. Because of their chemical instability, or because of the limited boiling range of hydrocarbons to which they are applicable, none of these is a universal solvent.

Use of ammonia, which is versatile and selective, was not discussed in earlier studies because the plant investment cost was found to be relatively high. This was due to the need for high pressure equipment and different construction materials, e.g. since ammonia attacks copper and its alloys. However, utility costs for the ammonia process are much less than for other processes. Therefore, the additional capital investment required for the ammonia extraction plant may be worthwhile a) if a longer payout time is acceptable, or b) in the event of change in demand for aromatics, or c) if it becomes necessary to change to other feed stocks with a different boiling point range. Ammonia and its properties as a unique solvent are discussed in Section 3.

2.3.3. Solvent Recovery

The solvent recovery section of an extraction plant is the most costly installation and may account for approximately 70% of the total capital cost. Furthermore, up to 90% of the operating cost can generally be attributed to the recovery operation (29). Therefore, although most consideration tends to be given to the extractor design, recovery constitutes a major factor. The economics of overall solvent extraction are dependent upon the cost of solvent recovery.

Clearly, therefore, the least costly method should be used to remove the solvent. The most common method is distillation, but other methods involve evaporation, use of an anti-solvent, cooling to reduce the solubility, or chemical treatment of product with a reactant to remove the solvent. Some combinations of these methods can be advantageous.

Distillation recovery systems: Solvent recovery by distillation may involve either of two types of solvent i.e., a solvent which is lower boiling or a solvent which is higher boiling than the feed stock.

With a low boiling solvent, since it is recovered as a distillate, the recycled solvent does not necessarily have to be periodically distilled to purify it. However, if there is a possibility of azeotrope formation consideration must either be given to the effect of solvent impurities on extraction operation or an alternative recovery method must be found. A solvent with a higher boiling point than the feed stocks,and therefore with a minimum energy requirement, has to be cleaned up periodically since it is collected as bottom product and will contain some non-volatile components of the feed.

Compression distillation is another method for solvent recovery. It is of limited application since each

component of the ternary system should have the following characteristics:

(1) A low molecular weight to minimise the boiling point rise in the boiler;

(2) Good compression characteristics to avoid an excessive compression ratio;

(3) Good heat transfer characteristics for effective heat transfer with a low temperature gradient; and

(4) Low heat of vaporization to reduce the equipment and operating costs.

Wash Oil Solvent Recovery System: This type of recovery system involves the application of liquid extraction to the extract using a wash solvent. A suitable wash solvent should clearly be immiscible with the solvent, have a favourable distribution coefficient and be easily separable from the extract by distillation or other means. Alternatively, it may be possible to wash the solvent out of the extract, but this is likely to be uneconomical if the solvent to feed ratio of the primary extraction process is too high.

Cooling Solvent Recovery Method: From energy consumption considerations the cooling solvent recovery system is the cheapest solvent recovery process.

This process can be applied to systems which are not heat sensitive and which may not be recovered by other means. The following characteristics should be met for

proper utilization of a cooling process.

1. (i) The solubility-temperature relationship of the solvent-hydrocarbon system should exhibit a rapid decrease in solubility with lowering of temperature.

   (ii) The physical properties of the phases should be such that settling of the phases at low temperatures is not difficult.

   (iii) A low specific heat of the solvent is desirable since the heat loads of the system are directly affected by the heat capacity of the solvent and the hydrocarbons and the solvent stream is generally the greater portion of the flow.

3. Ammonia as a Solvent in Petroleum Refining

Liquid Ammonia is a useful solvent with physical properties and selectivities suitable for the effective separation of several hydrocarbons. Its potential for use as a solvent was known as early as 1870. Extensive studies over the past 30 years have demonstrated that anhydrous ammonia and modified ammonia solvents have numerous advantages over other solvents. For those hydrocarbons for which its solvency is too low, a low molecular weight amine, such as monomethylamine is a good prosolvent to increase the solubility. When its solvency becomes too high, e.g. with aromatic hydrocarbons, water can be added as an anti-solvent. Solubility can also be controlled by the adjustment of temperature. In general other solvents for hydrocarbon separation tend to be limited in use because of their unsuitable temperature and solubility characteristics. The design and operation of apparatus with liquid ammonia as solvent and the analytical procedures used in solubility and phase equilibrium studies with it and with modified solvents were developed by Kirk (30).

In general, hydrocarbons and ammonia, or modified ammonia type solvents, form solutions with an upper critical temperature. Their solubility characteristics are represented by Figure 3.1. Curve DBM represents the composition of the ammonia-rich phase and curve ECM the composition of the hydrocarbon-rich phase. Point M is the maximum on the

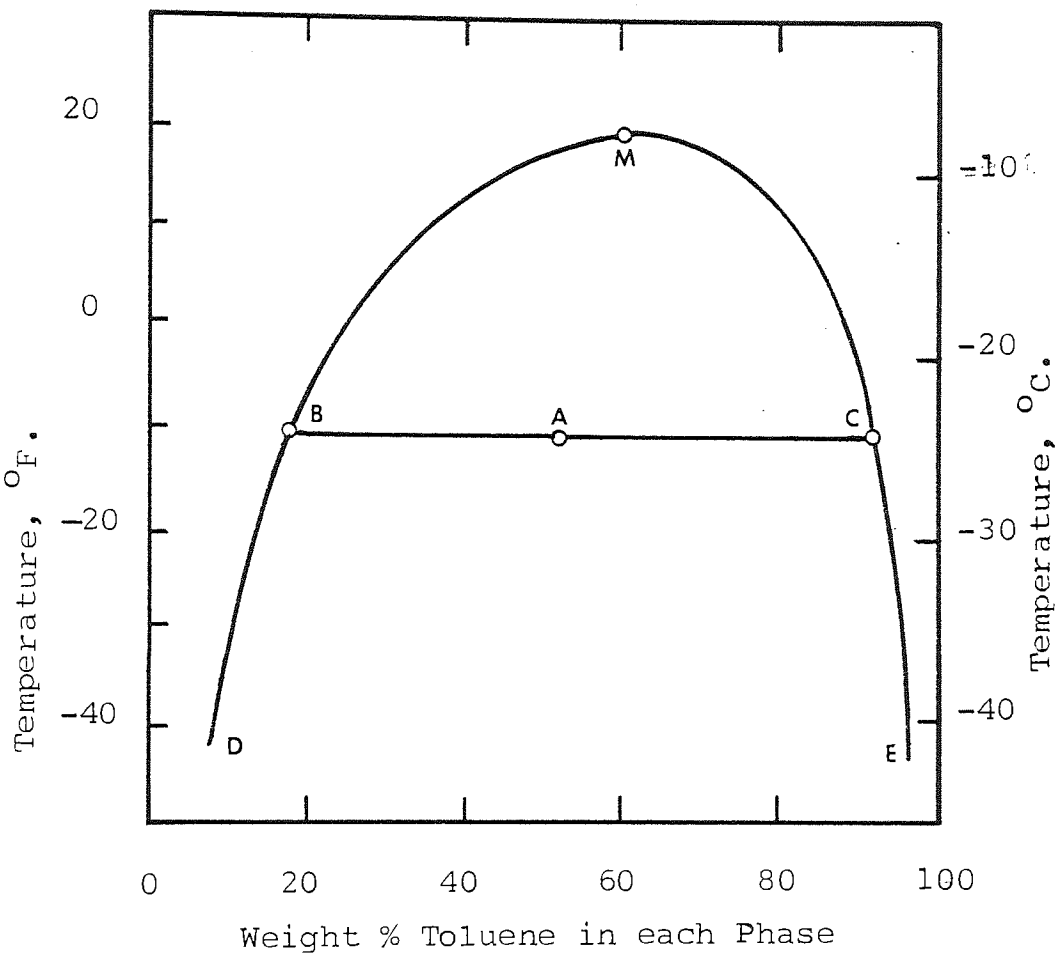


Figure 3.1

SOLUBILITY OF TOLUENE IN LIQUID AMMONIA

(B.A.C. = Typical tie line - mixture of composition A)

solubility curve. Two discrete phases cannot exist above this point. If the logarithm of the equilibrium concentration is plotted against the reciprocal of the absolute temperature a straight line is obtained at low solute concentrations.

3.1 Properties as a Solvent

Solubility-temperature data have been presented for a number of hydrocarbons in anhydrous ammonia by Francis (17). The following conclusions could be drawn from this data.

(a) With any given molecular type hydrocarbon, e.g. paraffin, aromatic or naphthane, there is a decrease in solubility with increasing molecular weight.

(b) For any given molecular weight, solubility increases in the order: paraffin, naphthanes olefins, cyclic olefins, diolefines, mononuclear aromatics and dicyclic aromatics. Hence less-saturated hydrocarbons are more soluble in ammonia.

(c) For any given molecular weight of a chain type compound, solubility increases with an increase in the degree of chain branching.

(d) Within the solubility range of 10 to 23 wt.% hydrocarbon at ordinary temperatures, an increase in temperature of $17^{o}C$ approximately doubles the solubility (31).

It was shown by Healy (32) that if the hydrocarbon type and the normal boiling point are known, the temperature

for a given solubility of hydrocarbon in ammonia can be predicted. Figures 3.2, 3.3, 3.4 show the temperatures for 5, 10, 15 wt.% solubility of various hydrocarbons. These correlations are useful for choosing the maximum boiling point range hydrocarbons which could effectively be extracted with ammonia solvents. For example, in the extraction of aromatics from a feed containing paraffins and naphthanes and with a lowest boiling point of 43°C and 10% solubility from Figure 3.3, at 38°C i.e. 100°F, the aromatic of about 212°C boiling point would have the same solubility as napthane boiling at about 95°C. Therefore, aromatic of 212°C boiling point would have the same solubility as naphthane boiling at about 95°C. Hence, an aromatic of 212°C boiling point and a naphthane of 95°C boiling point are not separable by extraction using liquid ammonia. Further, if the hydrocarbon contains a paraffin boiling at about 40°C the solubility of the paraffin at 32°C, i.e. 90°F, would be identical with that of aromatics boiling at 205°C. Thus, it would be impossible to separate an aromatic boiling at 205°C from a paraffin boiling at 40°C. Therefore, the maximum boiling range for which separation of paraffins from aromatics could be made is 40°C to 205°C.

Criswell (33) correlated solubilities with the molecular structural variables, such as number of carbon atoms, number of olefin double bonds and number of aromatic rings. Each of these structural characteristics affect

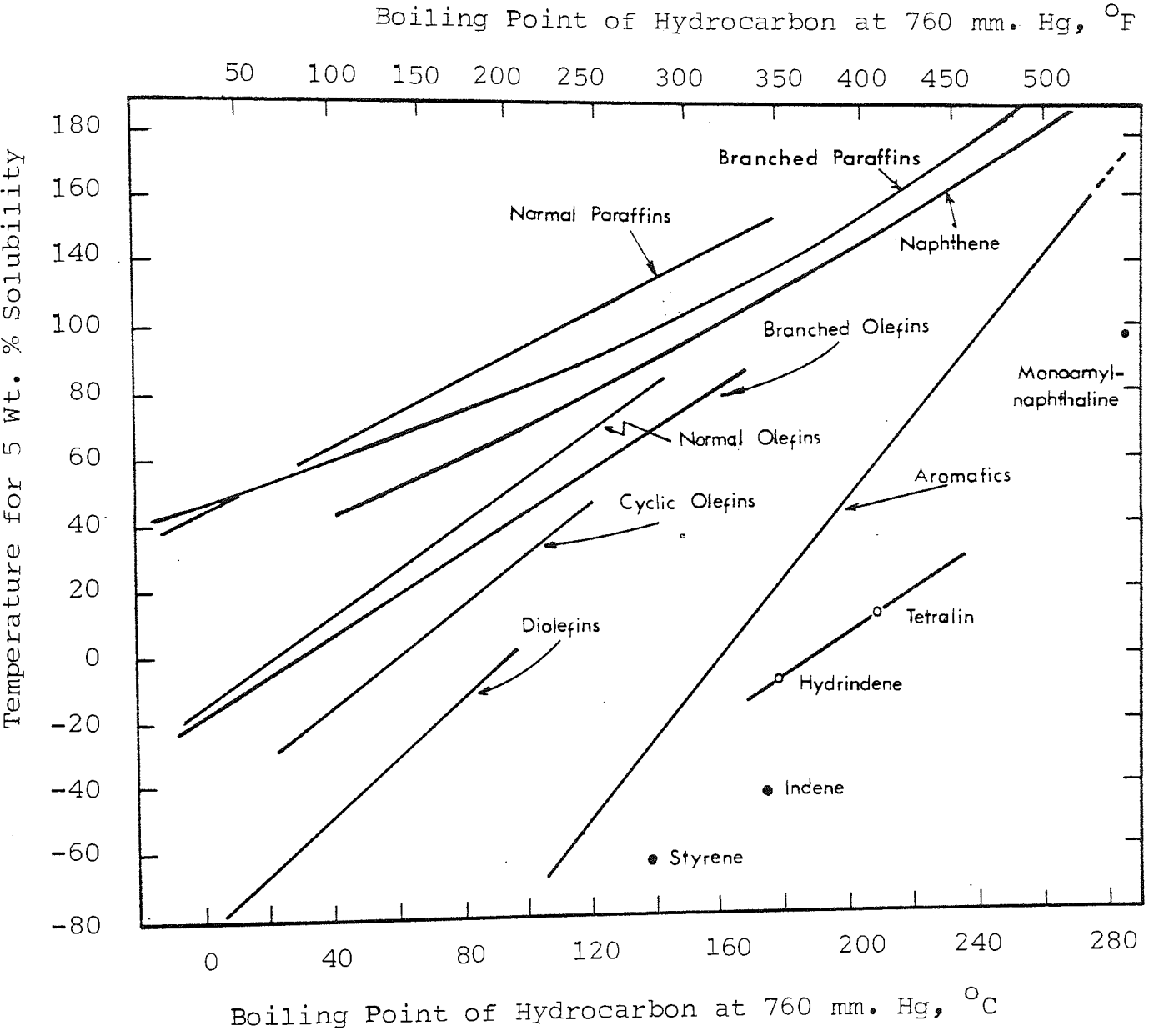


Figure 3.2

TEMPERATURE FOR 5 Wt. % SOLUBILITY OF VARIOUS HYDROCARBONS IN AMMONIA

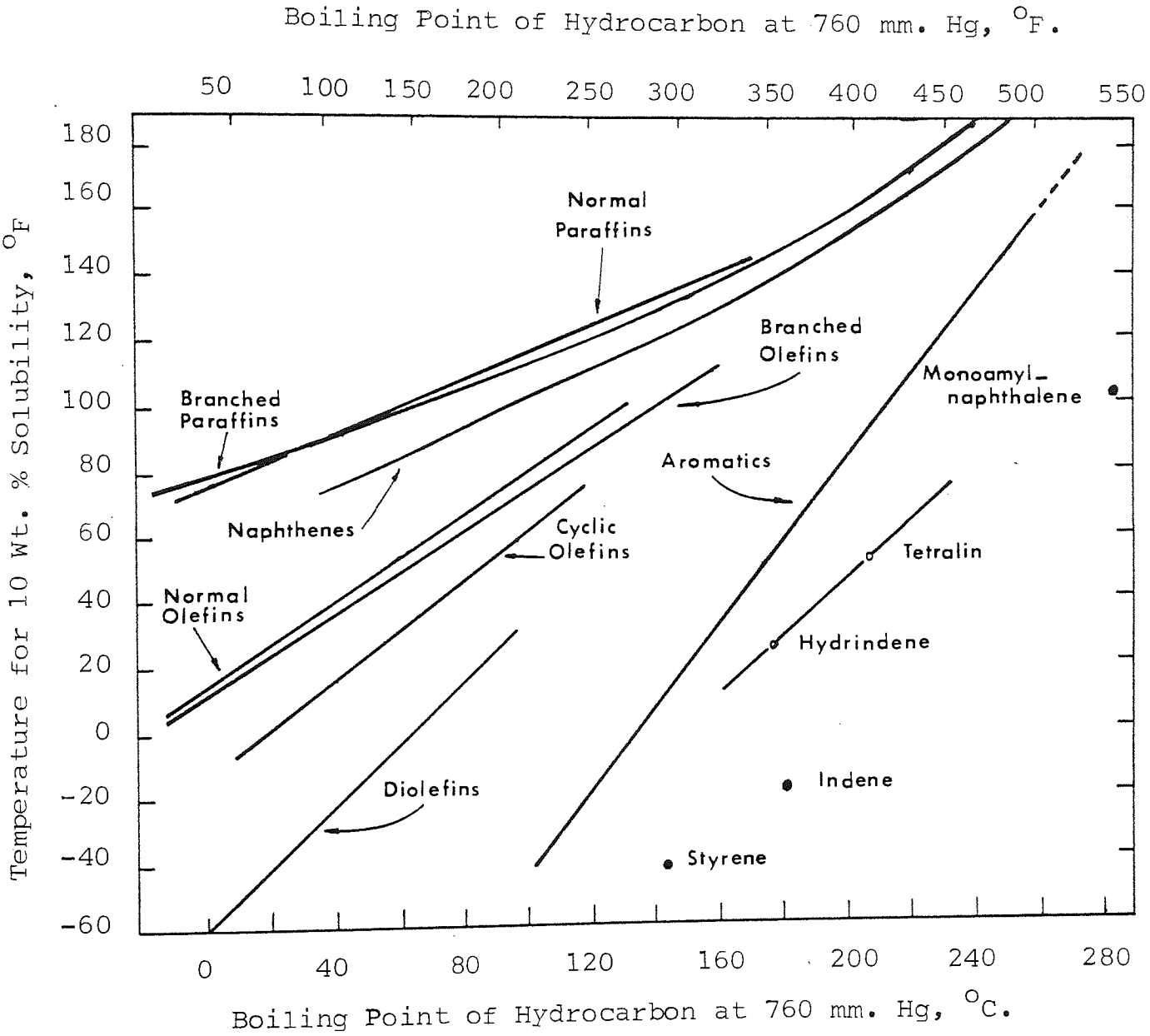


Figure 3.3

TEMPERATURE FOR 10 Wt. % SOLUBILITY OF VARIOUS HYDROCARBONS IN AMMONIA

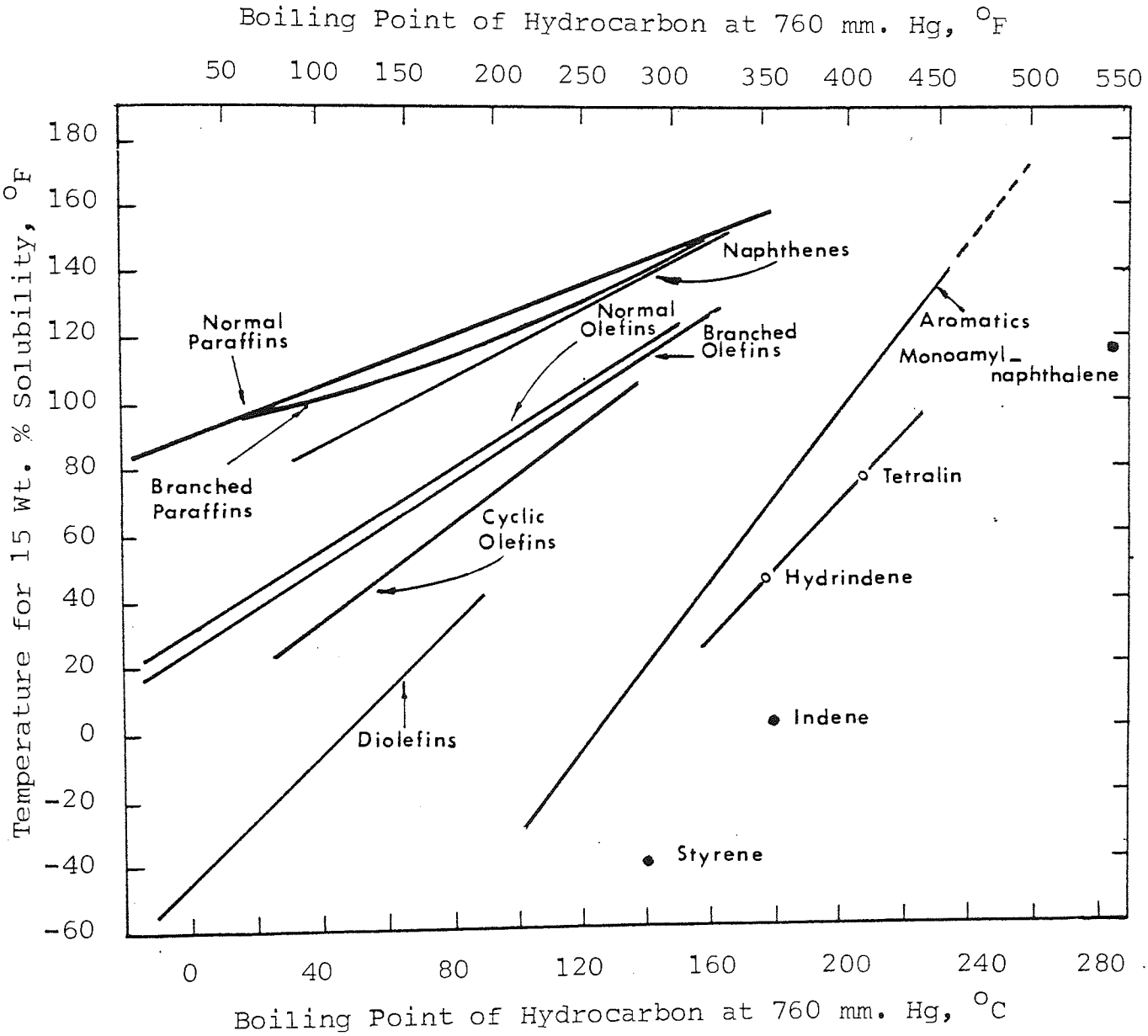


Figure 3.4.

TEMPERATURE FOR 15 Wt. % SOLUBILITY OF VARIOUS HYDROCARBONS IN AMMONIA

the solubility and each has a structure number which is proportional to the power of the various structural components of the molecule to increase or decrease the solubility temperature. The structural number of a molecule is the sum of the structure numbers of the various structural components. The molecular structural numbers have been tested by Braun (34). Correlations of structure numbers and temperatures for 5, 10, 15 weight % solubilities in anhydrous ammonia are plotted in Figure 3.5.

Ternary Equilibrium Data

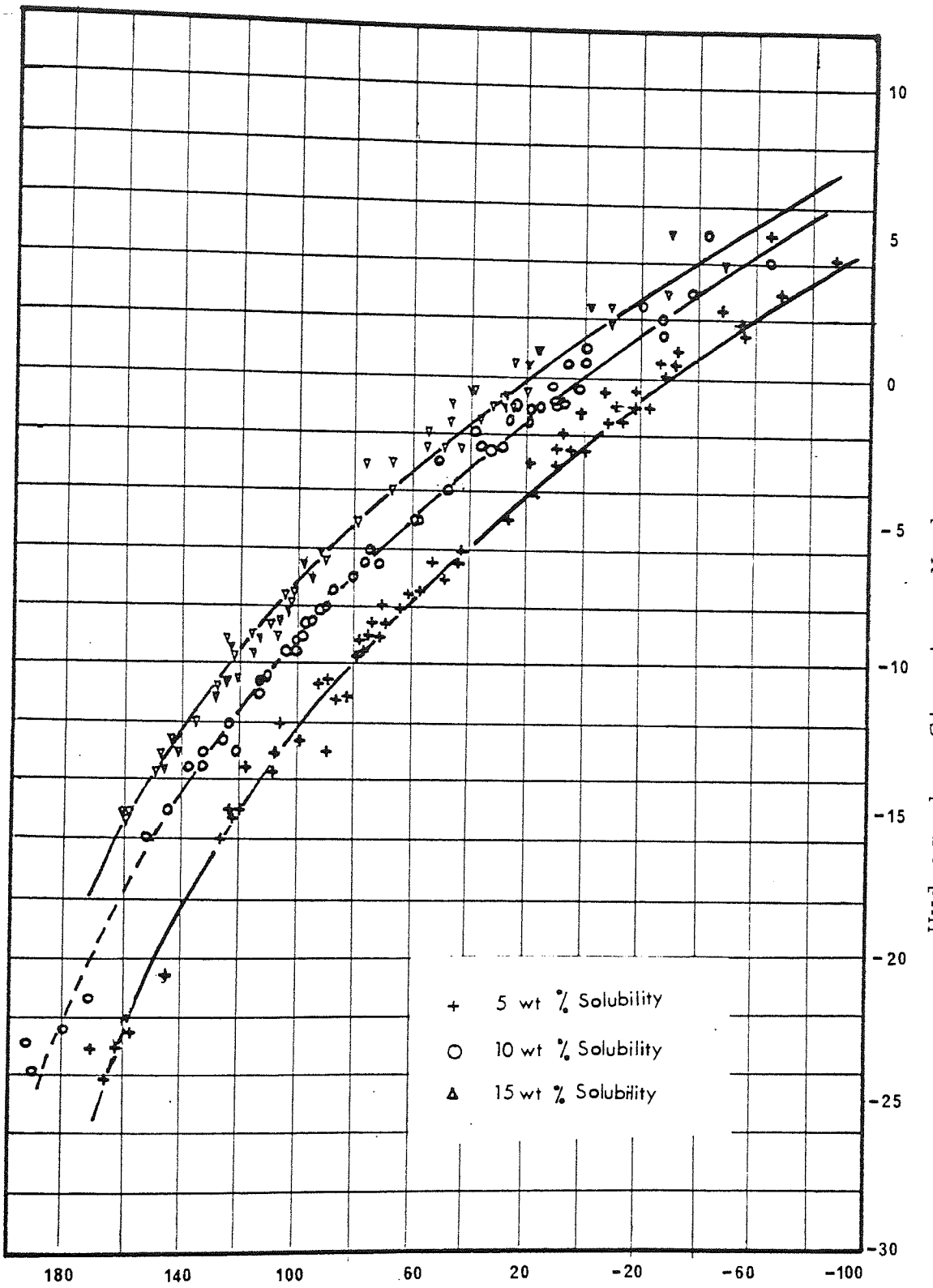
Apart from the solubility data for hydrocarbons, ternary equilibrium data are also necessary for extraction studies.

Ternary equilibrium data can be obtained experimentally by adequately mixing solvent with the hydrocarbon in e.g. a Smith-Bouner Cell and then separating into two phases for analysis. The composition of each phase is determined. These compositions are then represented on the triangular diagram. The ternary diagram for a typical system; Toluene-Methylcyclohexane-Ammonia, is given in Figure 3.6.

Selectivity

The selectivity, β , representing the composition of phases in equilibrium is not always constant for hydrocarbon-ammonia systems. The value of β generally depends

Temperature for 5, 10 and 15 Wt. %
Hydrocarbon Solubility ^{o}C



Temperature for 5, 10 and 15 Wt. %
Hydrocarbon Solubility ^{o}F

Figure 3.5

CORRELATION OF SOLUBILITY TEMPERATURE VERSUS
STRUCTURE NUMBER FOR HYDROCARBONS IN AMMONIA

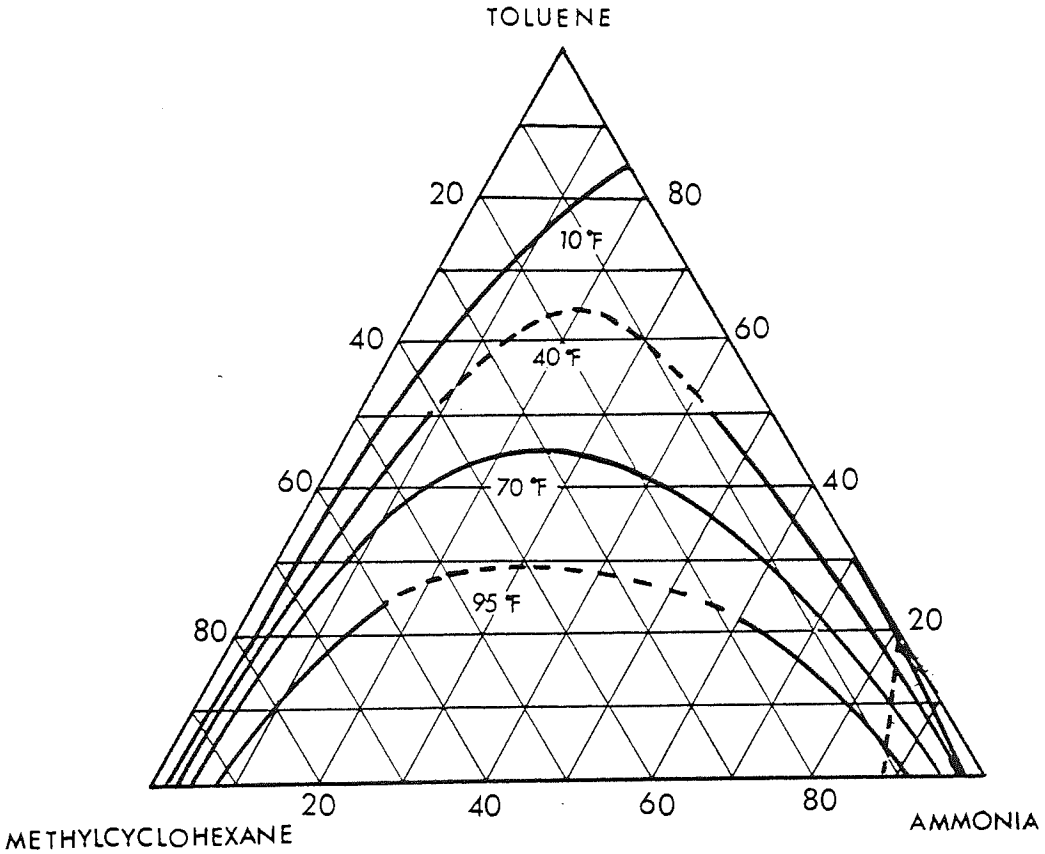


Figure 3.6.

EQUILIBRIUM RELATIONSHIP AT VARIOUS TEMPERATURES

The System: Toluene-Methylcyclohexane-Ammonia

on,

a) Solubility of the hydrocarbon in the solvent

b) The temperature,

c) The composition of the dissolved hydrocarbon. The effect of these variables for binary hydrocarbons with ammonia has been discussed by Cummings (35).

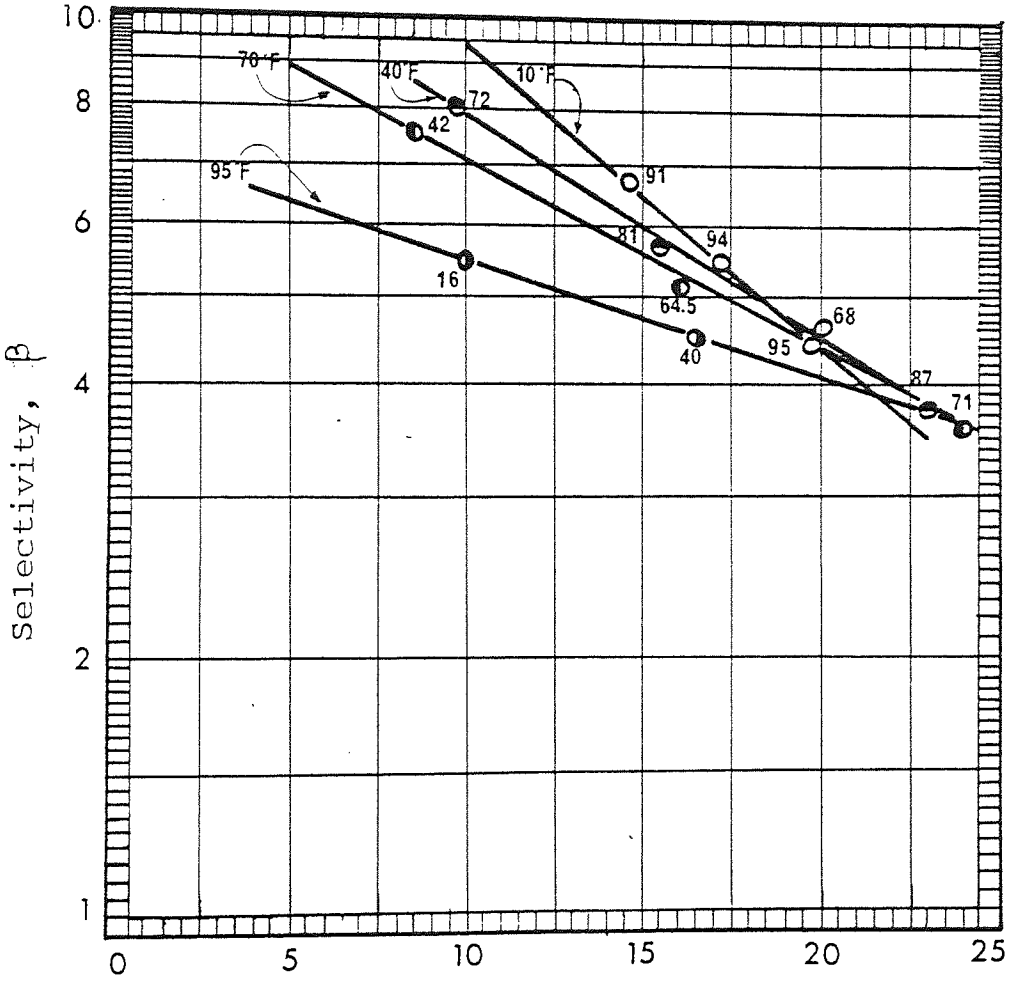
The solubility of the hydrocarbon dissolved in the solvent is the most important single factor affecting the selectivity. The selectivity of the solvent is greatest at low concentrations of solute. As the solvent concentration is increased the selectivity decreases. For extraction solvents the logarithm of β is plotted against hydrocarbon solubility in Figure 3.7. Since the selectivity varies with the hydrocarbon solubility it can be concluded that the selectivity decreases with increasing temperature because of the increased hydrocarbon solubility. However, there is another apparent effect of temperature on the selectivity. Temperature change affects the fields surrounding the solvent molecules causing the selectivity to vary. In summary, lower temperatures result in higher selectivities as shown in Figures 3.7 and 3.8.

Healy (32) correlated selectivity with the difference in temperature required for 10 weight % solubility for each hydrocarbon of a binary in liquid ammonia. The greater the difference in temperatures to maintain a 10 weight % solubility, the greater the selectivity. This

Figure 3.7.

EFFECT OF HYDROCARBON SOLUBILITY IN THE EXTRACT PHASE ON THE SELECTIVITY FACTOR, β.

System: Toluene-Methylcyclohexane-Ammonia



correlation is illustrated in Figure 3.8. Criswell (33) presented a relationship between the selectivity factor and the difference in hydrocarbon structure numbers. This is shown in Figure 3.9.

These two methods can be used to estimate the selectivity factor for mixtures of hydrocarbons.

Another factor which influences the selectivity is the dissolved hydrocarbon composition in the extract phase. It was found experimentally that the effect of hydrocarbon composition on the selectivity is not as important as the solubility or temperature (32, 36). However, at constant temperature selectivity factor, β, decreased slightly with increasing weight % of solute concentration in the extract phase.

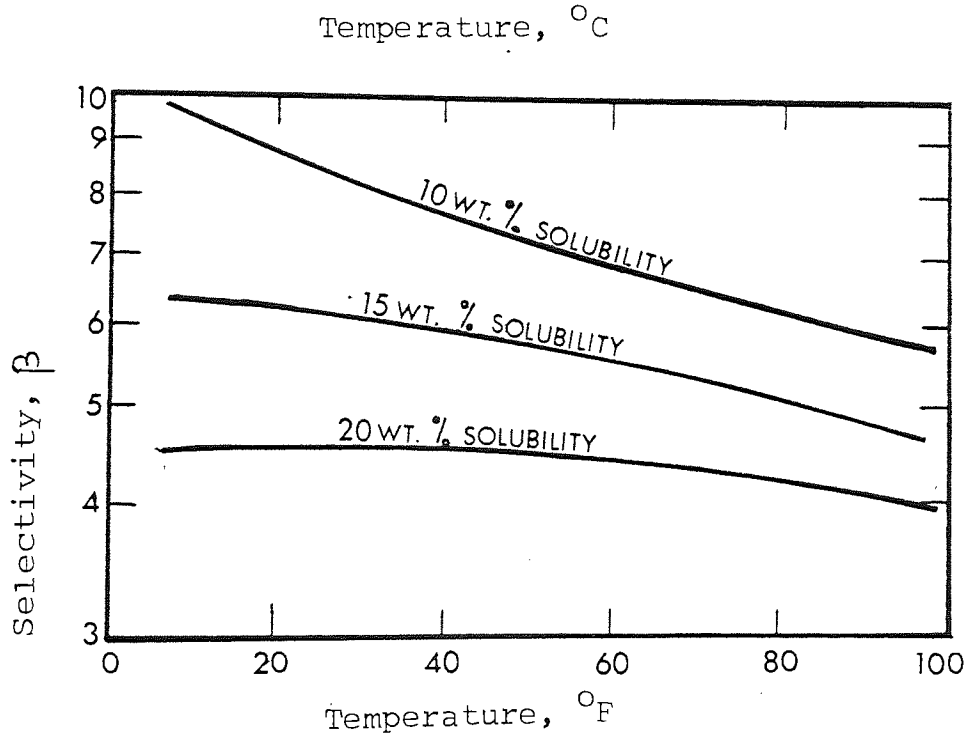
3.2. Modified Ammonia Solvents

The solubility of liquid ammonia can be modified to enable it to be used in cases where solubility is otherwise too high or too low. Solubility varies widely for different types of hydrocarbons. Because the selectivity of the solvent is dependent on solubility it is necessary to control the solubility of hydrocarbons in anhydrous ammonia.

Figure 3.8

VARIATION OF β WITH TEMPERATURE

System: Toluene-Methylcyclohexane-Ammonia



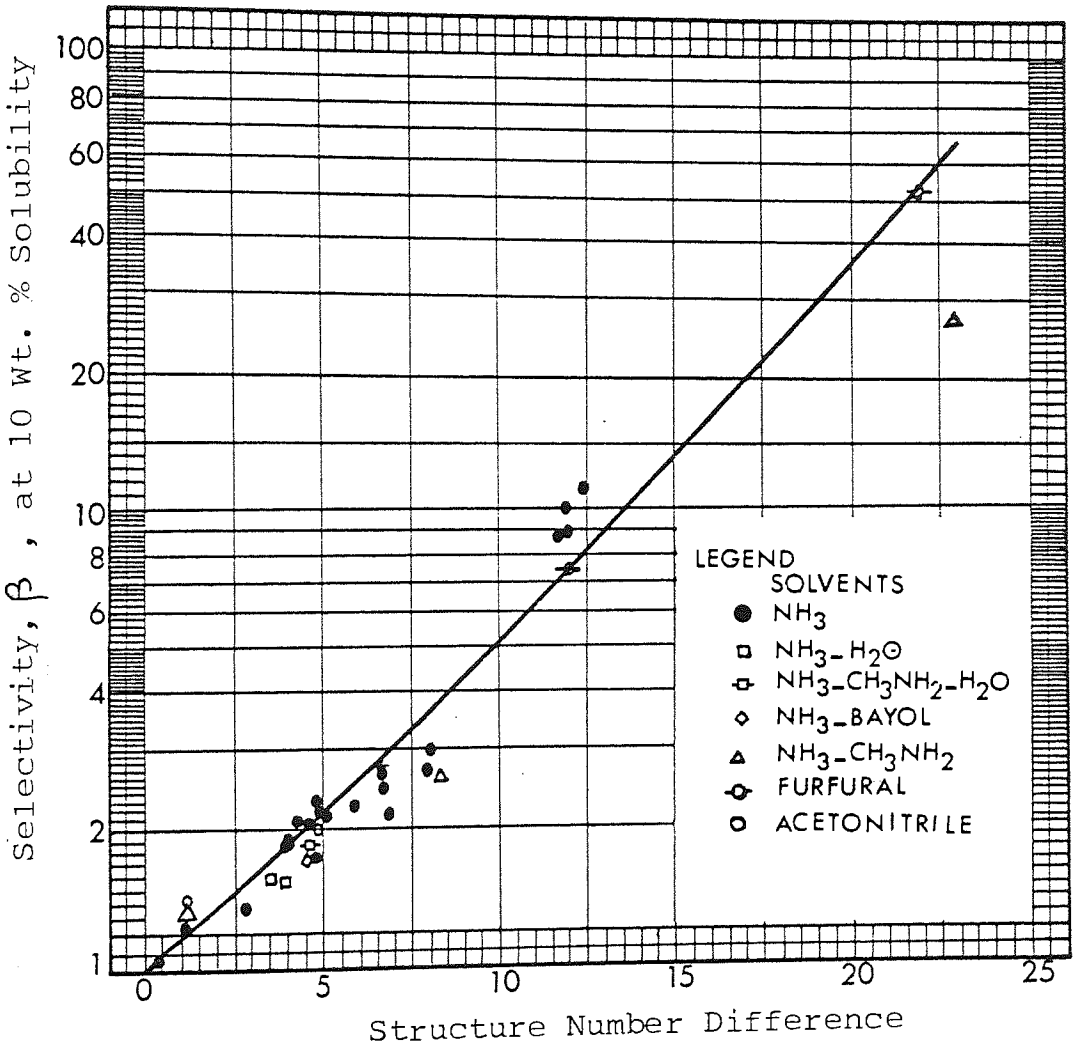


Figure 3.9.

CORRELATION OF SELECTIVITY FACTOR, β , AND DIFFERENCE IN HYDROCARBON STRUCTURE NUMBER

those of high polarity, such as aromatics, have high solubilities in anhydrous ammonia. Their solubility in the solvent can be decreased using an antisolvent. There are a number of antisolvents which can be used with ammonia such as ethylene glycol, formamide, water and ethylene diamine (37). Water is the most satisfactory of these because it is cheap, readily available, and easy to handle in a solvent recovery unit. However, since low temperatures are achieved in ammonia flashing, care must be taken in design of the solvent recovery unit. Very low water concentrations in ammonia solvents are effective; therefore the desirable physical properties of ammonia are unaffected. Other antisolvents have less effect on solubility when used in small amounts, so that they must be used in higher concentrations in the solvent (34).

Solubility Temperature Data

Analyses by Criswell (33) and Healy (32) for a number of hydrocarbon pairs in ammonia-solvents indicated that the solubility-temperature relationships for hydrocarbons in ammonia-solvents containing small amounts of water differed little from the solubility temperature relationship with anhydrous ammonia alone. For hydrocarbon concentrations less than 40% the solubility curves are simply shifted towards a higher solubility temperature with no change in the slope. At a constant hydrocarbon solubility, in the range of 10-30 weight %, addition of 10 weight % water

to ammonia increases the solubility temperature by about $4^{o}C$. If constant temperature is taken as a basis, at a constant hydrocarbon solubility below 40 weight % the addition of 4-5 weight % water to the solvent will halve the solubility.

Ternary Equilibrium Data

The effect of water as an antisolvent to ammonia is shown on the triangular diagram in Figure 3.10. The data represented in this figure is analogous to that in Figure 3.6 where the solvent is anhydrous ammonia but the temperature varied for different solubilities. However, instead of the solubility being reduced by a temperature reduction it is reduced by water addition.

Selectivity

The addition of small amounts of water, up to 10% has little or no effect on selectivity. Therefore the selectivity correlations given previously also apply to ammonia-water solvents.

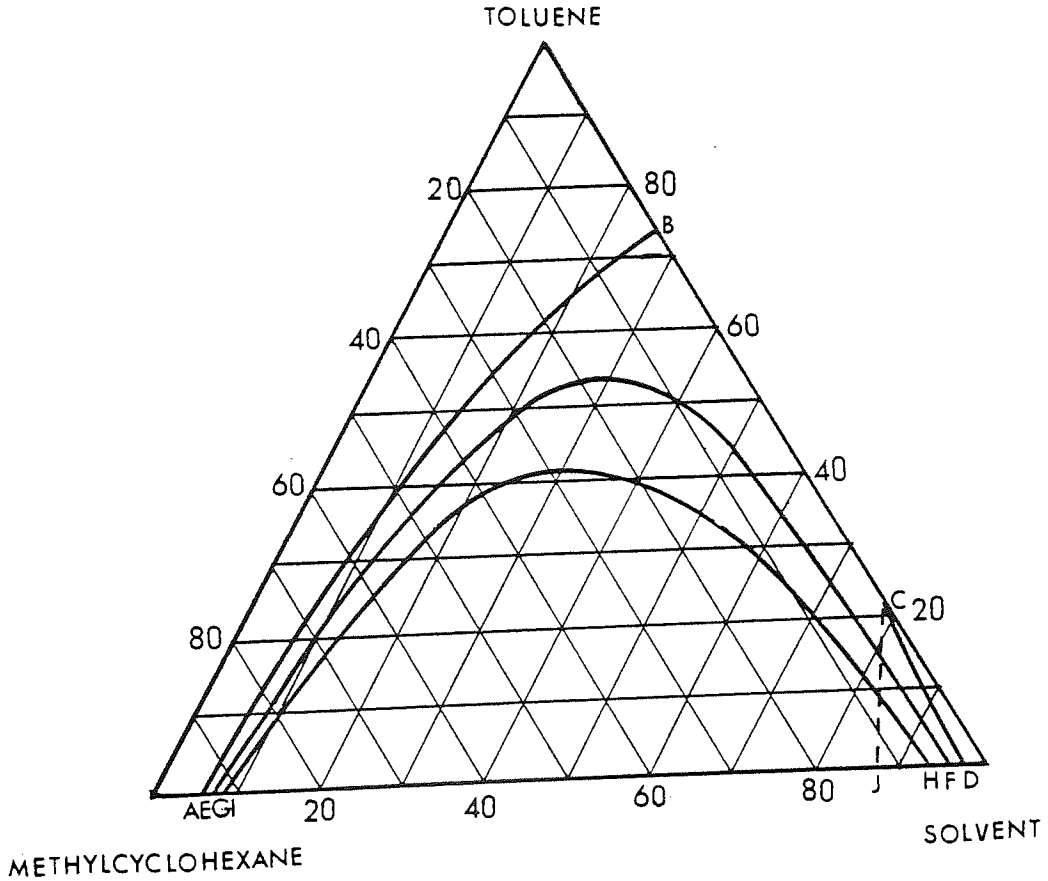
3.2.2. Ammonia with a Pro-solvent

High molecular weight hydrocarbons generally have low solubilities in liquid ammonia. In practical extractions this low solubility would necessitate use of high solvent to oil ratios resulting in high operating costs. The solubility could be increased by high temperature

Figure 3.10

EQUILIBRIUM RELATIONSHIP FOR THE SYSTEM:

Toluene-Methylcyclohexane-Aqueous Ammonia



Area	Solvent Comp., Wt. % NH_3	H_2O
AB-CD	86	14
EF	90	10
GH	95	5
IJ	100	0

operation but this is not practical since it would require high pressure equipment and hence increased capital investment. The addition of a prosolvent is a better method of increasing the solubility. The prosolvents which could be used with ammonia are high glycols, ethers and ether alcohols, methanol and other alcohols, amines, aniline, pyridine, the methylamines, other low molecular weight aliphatic amines, phenol and toluene. Among these mono-methylamine is most useful because of the ease of recovering it from the extract and raffinate streams together with ammonia in distillation columns (34).

Solubility Temperature Data

Long (36) and Criswell (33) both obtained data on the solubilities of hydrocarbons in ammonia-monomethylamine mixtures. The data for n-heptane - methylcyclohexane, shown in Figure 3.11 are typical of the solubility behaviour of hydrocarbons in this solvent. The solubility curves are nearly parallel. For the hydrocarbons studied, the addition of 20 weight % monomethylamine to ammonia increased the hydrocarbon solubility equivalent to that achieved by 17 to $23^{o}C$ temperature rise for pure ammonia (38). In summary the solubility of hydrocarbons can be doubled by the addition of 20 weight % monomethylamine to ammonia.

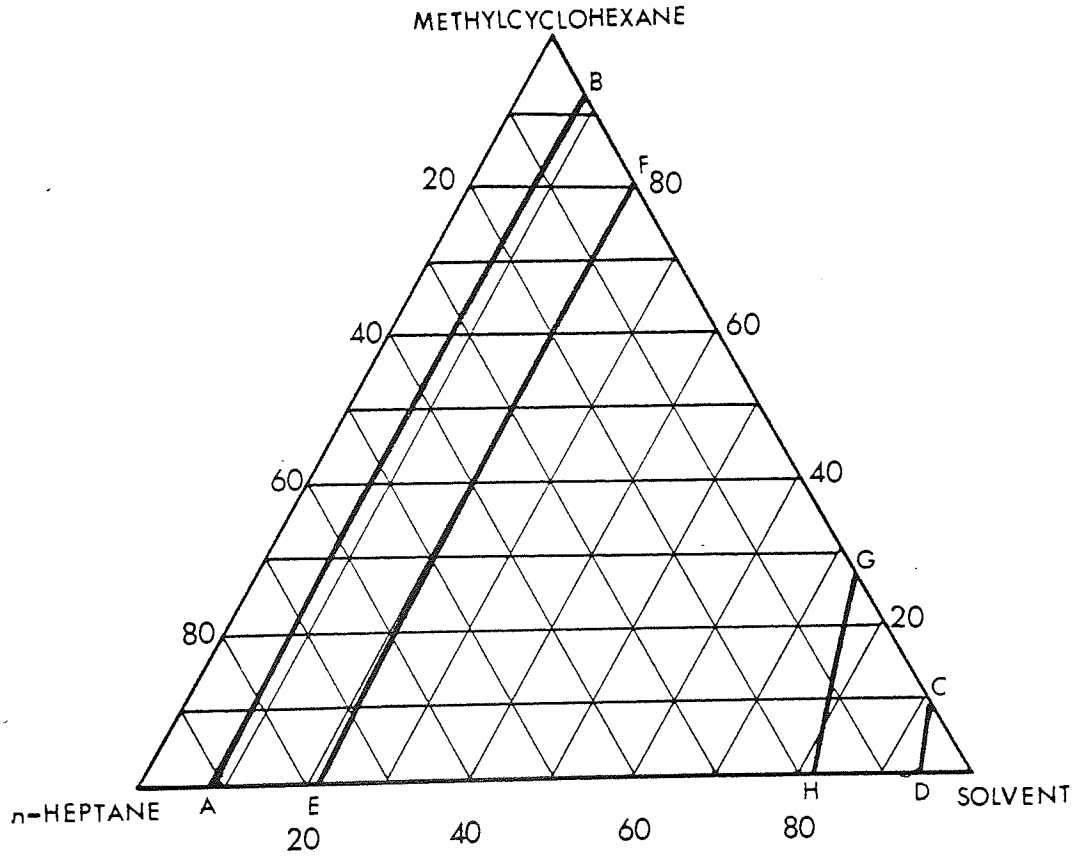
Ternary Equilibrium Data

The effect of addition of monomethylamine to ammonia

Figure 3.11

EQUILIBRIUM RELATIONSHIP FOR THE SYSTEM:

Methylcyclohexane-n-Heptane-Ammonia/Methylamine



Area	Weight % NH_3	Weight % MMA	Approx β
AB-CD	100	0	1.3
EF-GH	73	27	1.3

is shown in Figure 3.11 for the system methylcyclohexane-n-Heptane, and solvent. The solubility is increased from CD to GH by the addition of 27 weight per cent monomethylamine.

Selectivity

Addition of monomethylamine, or another prosolvent, to ammonia does not change the selectivity considerably. Therefore, the correlation for selectivity with pure ammonia can be used for the monomethylamine-ammonia system with little loss of accuracy.

3.2.3. Ammonia-Monomethylamine-Water

The use of an antisolvent with the mixed solvent ammonia-monomethylamine provides greater flexibility to the system. The solvent can then be used for a wider variety of feed stocks than any other solvent in current use for hydrocarbons extraction.

The relationship between the solubility of n-heptane and the composition of the ternary solvent is presented by Braun (34). Similar data were obtained by Criswell (33) for m-xylene and octane 1. These data proved that at constant solubility and constant temperature the equivalence factor between monomethylamine and water is about 3.5 or 4.0 to 1.0. That is the prosolvent effect of 20 weight % of monomethylamine would be neutralised by the addition of 5. - 5.5 weight % water. Moderate amounts of methylamine

and water in anhydrous ammonia do not affect selectivity of anhydrous ammonia. Ternary equilibrium diagrams for several systems using ammonia modified with water and monomethylamine as a solvent have been published by Criswell (33).

3.3 Practise and Limitations

Various selective solvents or solvent mixtures can be used in the separation of mineral oils, such as petroleum oils, containing various types of hydrocarbons such as paraffinic, aromatic, hydro-aromatic, or naphthanic and unsaturated structures having a wide range of molecular weights.

In the separation of viscous oils organic solvents like phenol, furfural, cresols, nitrobenzene, aniline, or dichlorodiethyl ether, are used due to their preferential selectivity for relatively more aromatic type compounds. The use of solvents other than organic solvents have been suggested in order to separate some desirable constituents from lower boiling petroleum fractions. Particular solvents for an efficient and economic separation of feed mixtures are liquified inorganic solvents such as liquid sulphur dioxide and anhydrous liquid ammonia.

Liquid sulphur dioxide even with the addition of a modifying agent, has limited use due to the low purity of the extract even at very low temperatures. The organic solvents mentioned earlier are satisfactory for lubricating

oil extraction and high molecular weight separation, but are unsuitable for the treatment of lighter hydrocarbons.

Although it is possible to alter the solvent power by addition of other liquids, the effectiveness of these modifying agents depends mainly on the properties and the characteristics of the primary solvent to which they are added. For most solvents there are only a few modifying agents, due to the creation of unsuitable density factors, emulsion formation and mutual solubility, chemical interaction and corrosion problems. Some of these combinations cause some unexpected difficulties. For example the addition of benzol to sulphur dioxide, which increases the solvent power considerably, reduces the selectivity. Addition of water to phenol reduces its solvent power but phenol-water mixtures are more corrosive than either phenol or water alone. Solubility of hydrocarbons in furfural and Chlorex cannot be controlled by the addition of modifying solvents because both are chemically reactive. Although liquid sulphur dioxide is a good solvent for aromatics separation, very few liquids are soluble in liquid sulphur dioxide without chemical reaction or causing corrosion problems in the equipment. Furthermore no modifying agents have been found to change the dissolving power of sulphur dioxide without reducing its selectivity. In general use of modifying agents for changing solvent power is restricted in application because of the disadvantages e.g. loss of selectivity, increase in corrosiveness, the production of

emulsions, difficulty in separating the modified solvent and the primary solvent from the hydrocarbon mixture and the incompatibility of the modifying solvent with the primary solvent over a wide range of concentration or hydrocarbon solubility.

As described earlier use of modifying solvents, together with temperature control, permit the solvent power of ammonia to be altered over a wide range to suit the specific mixtures being extracted. These solvents can be removed from the final product and recovered fairly easily. They do not form waste tarry residues. Further,high temperature equipment is not required even for the complete removal of solvent from the final product.

The versatility of liquid ammonia with modifying solvents has been studied extensively (30, 36) using a mixer-settler type reciprocating extractor. The extraction feeds included virgin naphthanes,catalytic and thermally reformed naphthas ,catalytic and thermally cracked naphthas ,kerosenes, distillate oils, catalytic oils and narrow-boiling hydrocarbon concentrates. The boiling points of the hydrocarbons in these feeds ranged between 40° to 600 °C. The extraction products ranged from high purity petrochemicals such as benzene, cyclohexane, and durane to complex hydrocarbon mixtures including high octane automotive and aviation fuels, diesel fuels with high octane number, jet fuels and heating oils with improved burning characteristics and high heat content, improved cracking stocks and

refined lubricating oils with high viscosity indices. By liquid ammonia extraction it was possible to isolate in a high state of purity all the major hydrocarbon types found in refinery streams like polynuclear aromatics, mononuclear aromatics, olefins, naphtanes ,and paraffins.

In the separation of polynuclear aromatics and mononuclear aromatics from virgin naphtas ,catalytically reformed naphtha, catalytically cracked naphtha, and catalytic cycle oils the aromatic content in the extract could be up to 99% depending upon the conditions. However, in the extraction of aromatics from thermally cracked or thermally reformed, naphthawith a high boiling range and olefinic content or from high boiling virgin stocks like kerosines and lube oils, the aromatic content of the extract phase was less than 98%. At high solvent to oil ratios olefins, naphthenic and paraffinic products can be obtained at 99% purity using liquid ammonia with modifying agent as solvent.

Finally, cost estimates for the liquid ammonia extraction process have been compared with those for the use of ethylene glycol. The initial investment cost for the ammonia process was estimated at 1.5 times that of the ethylene glycol process. However, the operating cost was about 25% less which would mean that the ammonia process is favourable for longer pay out times. In addition, diethylene glycolhas limited applications because, with hydrocarbon feeds of boiling points of 205^{o}C and less there

is a possibility of gum formation. The ammonia process could be used for hydrocarbon feeds within the boiling point range 40^{o} to 600^{o}C. Therefore an extraction plant using ammonia as a solvent would be more flexible than any of the other practicable solvents.

4. The Rotating Disc Contactor

The Rotating Disc Contactor was first introduced by Reman (39). It was primarily used for the extraction of lubricating oils for which it was found to be ideal. Recently, it has been used extensively in industry owing to its versatility and other advantages. The RDC generally has a high efficiency, measured as a low HTU or HETS value. There is only limited loss of efficiency on scale up. Also the efficiency is maintained over a wide capacity range. This would facilitate the use of different feed stocks at different flow conditions and rotor speeds. Finally, the RDC is cheap and simple to build, and relatively economical to operate.

The RDC finds industrial use mainly in the petrochemical industries, especially in lube-oil extraction, in the extraction of merceptans, dechlorinization of hydrocarbons and similar processes. It was found to be ideally suited to the separation of lube-oils with flexibility in operation, lowered investment cost and low solvent to oil ratios resulting in low operating costs (39,40,41,42,43,44). The RDC has also been employed successfully in the extraction of mercaptans from gasoline fractions (18). Packed columns and mixer-settlers were found to be inefficient owing to the excessive height requirement with packed columns and the relatively high cost with mixer-settlers. The RDC made satisfactory separations possible at low investment and operating costs.

The RDC has been applied successfully to the extraction of mixed chlorinated hydrocarbons, giving a high efficiency and volumetric capacity compared with other extractors (45).

Its usefulness as an extractor has also been proved in the purification of synthetic detergents.

Its use overcame difficulties due to the formation of a gel-like emulsion which created problems in extraction (46) in mixer-settlers and packed columns. The RDC is also applied extensively to the extraction of oxygen compounds from fruit juices with alcohol, propane deasphalting (47,48, 49), phenol recovery (50) and extraction of caprolactam (51).

4.1. Construction and Operation of the RDC

The RDC consists of a vertical cylindrical shell divided into a number of compartments formed by a series of stator rings. A rotating disc is centred in each compartment and supported by a rotating shaft as shown in Figure 4.1. As in other countercurrent extraction columns, the lighter liquid enters the contactor at the bottom and flows upward while the heavier liquid, which enters at the top, descends. Either of the phases may form the dispersed phase and in most large diameter contactors initial dispersion of this phase occurs via a perforated plate or pipe ring. This eliminates the need

for some initial column height merely to achieve dispersion. Free space in the column, or external settlers, are provided at the top and the bottom of the column for the separation of heavy and light phases. Mass transfer efficiency is dependent on the drop size which is controlled by the use of an appropriate rotor speed. The flat profiles of the discs and the stators create a uniform shearing stress which favours creation of a relatively narrow drop size distribution. Any imperfection on the surfaces could cause very small drops to form which could reduce the volumetric capacity and create phase separation problems. The desired flow pattern of the drops in each compartment is shown in Figure 4.2.

The drops are influenced by four basic forces:

i. Rotation around the shaft induced by disc rotation;

ii. Centrifugal force applied by the disc rotation;

iii. Buoyancy force due to density difference causing the lighter liquid to rise, and;

iv. Swirl due to tangetial inlet of either or both of the phases.

The flow patterns of drops in the RDC depend upon the speed of rotation. Two general flow patterns were observed as illustrated in Figures 4.3(a) and 4.3(b). At rotor speeds below 1.5 m/s. (= 300 ft/min.) the dispersed phase droplets were trapped under the stator rings. The amount of entrapment was a function of the column geometry,

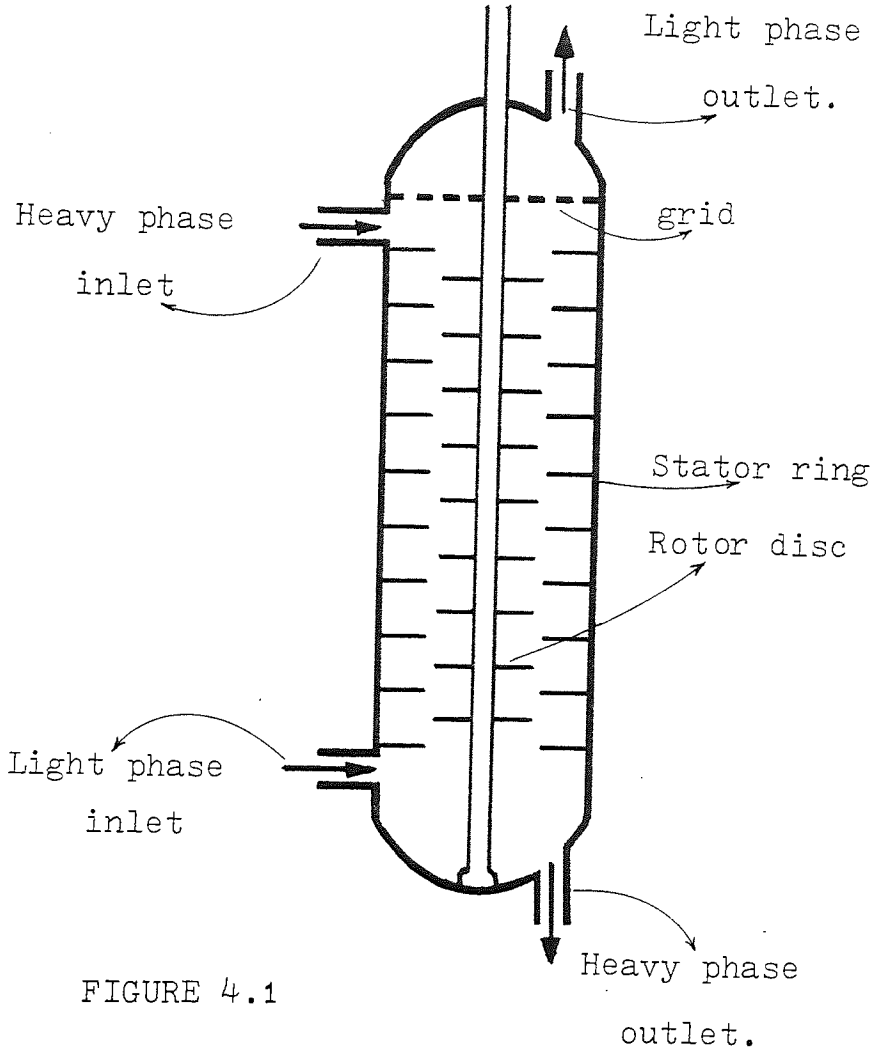


FIGURE 4.1

THE ROTATING DISC CONTACTOR

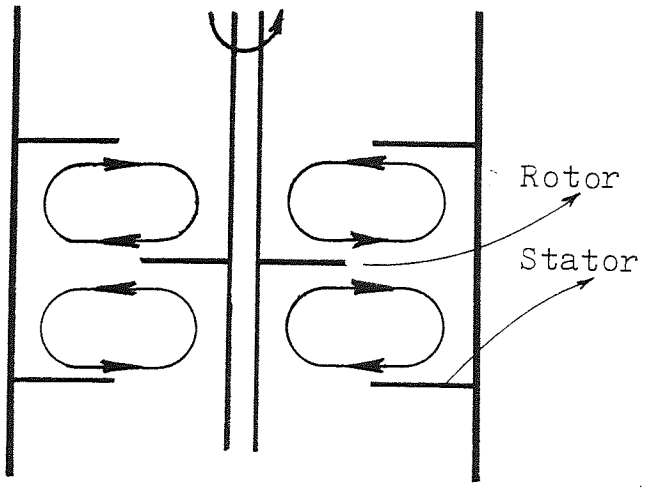


FIGURE 4.2

IDEALIZED FLOW PATTERN IN AN RDC

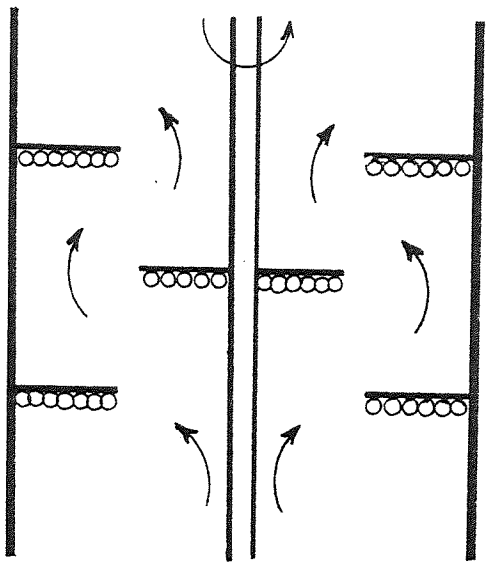


FIGURE 4.3(a)

DISPERSED PHASE FLOW PATTERN

PERIPHERAL SPEED. (<1.5 m/sec.)

System = Toluene - Water

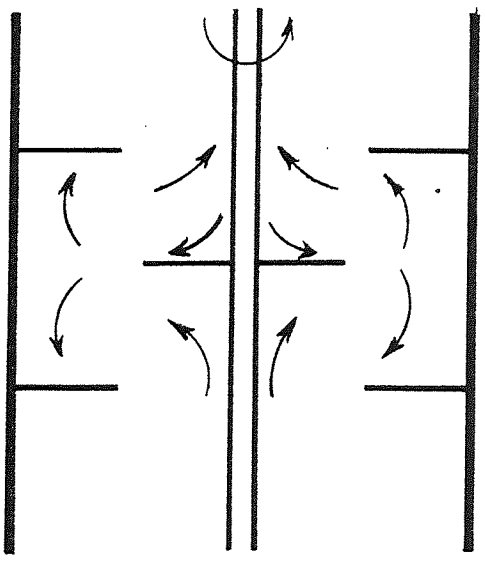


FIGURE 4.3(b)

DISPERSED PHASE FLOW PATTERN

PERIPHERAL SPEED. (>1.5 m/sec.)

rotor speed and liquid flowrates. At rotor speeds above 1.5 m/s. and also at flowrates near to flooding, the flow pattern was as shown in Figure 4.3(b). In this case back mixing had an increasing influence on extractor efficiency since it is a function of rotor speed and flow rates as well as column geometry.

The volumetric capacity of the RDC is greatly dependent on rotor speed and the geometry of the contactor.

The influence of these parameters on the capacity and efficiency of the contactor are listed in Table 4.1.

Increasing	Capacity	Efficiency
Rotor speed	decrease	increase
Disc diameter	decrease	increase
Stator ring opening	increase	decrease
Compartment height	increase	decrease

TABLE 4.1.

EFFECT OF OPERATING PARAMETERS ON RDC CAPACITY AND EFFICIENCY

In the selection of geometry for an RDC for a particular extractor duty, a choice may be made between a high efficiency - low capacity or a low efficiency - high capacity design. In general the optimum column dimensions are in the range (52);

$$\frac{\text{Stator Diameter}}{\text{Column Diameter}} \quad \left(\frac{S}{D}\right) = 0.66 \text{ to } 0.75$$

$$\frac{\text{Disc Diameter}}{\text{Column Diameter}} \quad \left(\frac{R}{D}\right) = 0.5 \text{ to } 0.66$$

$$\frac{\text{Compartment Height}}{\text{Column Diameter}} \quad \left(\frac{H}{D}\right) = 0.33 \text{ to } 0.5$$

As in other countercurrent extraction apparatus the efficiency of the RDC increases to some degree with increasing phase ratio.

4.2. Hydrodynamics and Design Criteria

The hydrodynamics and flow characteristics of the RDC have been studied extensively and numerous correlations have been developed to predict limiting volumetric capacity and to characterise extraction efficiency.

Mass transfer calculations are based on the primary equation:

$$N = K A \Delta c \qquad (4.1)$$

The coefficient mass transfer, K, depends on the rate of diffusion inside, at the interface , and outside the droplet. The overall coefficient is therefore related to the individual coefficients for the dispersed and continuous phases by;

$$\frac{1}{K} = \frac{1}{k_d} + \frac{1}{mk_c} \qquad (4.2)$$

This neglects any interfacial resistance.

The interfacial area, A, is a function of the dispersed

phase hold-up and the dropside distribution. The driving force depends on concentration gradients which are affected by the back-mixing characteristics of the RDC.

Dispersed Phase Hold-Up

The interfacial area is the product of the average size of the droplets and the number of the drops within the column; that is, the hold-up. The average drop size can be estimated from correlations related to physical properties of the fluids and operating parameters (44, 53, 54, 55) or it can be obtained by direct counts from high speed photographs in transparent columns. The dispersed phase hold-up is related to the superficial velocities of the continuous and the dispersed phases by equations:

$$V_s = \frac{V_d}{x_d} + \frac{V_c}{1-x_d} \qquad (4.3)$$

$$\bar{V}_N(1-x_d) = \frac{V_d}{x_d} + \frac{V_c}{1-x_d} \qquad (4.4)$$

The characteristic velocity, $\bar{V}_N$, is dependent on the geometry of the RDC and the physical properties of the system according to the relationship,

$$\frac{\bar{V}_N \mu_c}{\gamma} = 0.012 \left(\frac{\Delta\rho}{\rho_c}\right)^{0.9} \left(\frac{g}{RN^2}\right)^{1.0} \left(\frac{S}{R}\right)^{2.3} \left(\frac{H}{R}\right)^{0.9} \left(\frac{R}{D}\right)^{2.7} \qquad (4.5)$$

Equation (4.4) was later modified (56) to allow for variations in the geometry of the RDC. The modified equation included a constant K as:

$$\bar{V}_N(1-x_d) = \frac{V_d}{x_d} + \frac{K_1 V_c}{1-x_d} \qquad (4.6)$$

where, $K_1 \leq 2.1$ if $\frac{S-R}{D} \leq \frac{1}{24}$ or $K_1 = 1$ otherwise.

The $\bar{V}_N$ relationship was also modified to include $(\frac{R}{D})^{2.6}$ instead of $(\frac{R}{D})^{2.7}$

At rotor speeds less than 1.5 m/s. the characteristic velocity $\bar{V}_N$ was found to remain constant, while at higher speeds $\bar{V}_N$ was correlated by; (4.7)

$$\frac{\bar{V}_N \mu c}{\gamma} = K_1 \left(\frac{\Delta\rho}{\rho_c}\right)^{0.9} \left(\frac{g}{RN^2}\right)^{1.0} \left(\frac{S}{R}\right)^{2.3} \left(\frac{H}{R}\right)^{0.9} \left(\frac{R}{D}\right)^{2.6}$$

where K_1 had the value 0.012 at $\frac{S-R}{D} > \frac{1}{24}$ and 0.0225 at $\frac{S-R}{D} \leq \frac{1}{24}$

A further modification of equation (4.6) incorporated allowance for coalescence and break up of droplets (64).

$$\frac{V_d}{x_d} + \frac{V_c}{1-x_d} = \bar{V}_N(1-x_d)\exp(x_d(Z/M - 4.1)) \qquad (4.8)$$

Z is the coefficient of coalescence and was correlated with Reynolds number by:

$$Z = 1.59 \times 10^{-2} \left(\frac{D}{\mu_c}\left(\frac{\gamma}{\rho_c d_o}\right)^{\frac{1}{2}}\right)^{\frac{1}{2}} \qquad (4.9)$$

However, it has been observed that the hold-up does not remain constant throughout the column length. Therefore, in a further study (58) the hold-up profile was obtained considering the break up of drops and longitudinal mixing of the dispersion.

Capacity of the RDC

The effect of the geometry and rotor speed of the RDC on the volumetric capacity is shown in Table 4.1. For each flowrate of one phase, there is a corresponding maximum flowrate of the other phase. The maximum capacity of the column is then determined by 'flooding' which occurs when one of the phases is rejected by the column.

Flooding flowrates of both phases are calculated by setting $(\frac{\partial V_d}{\partial x_d})_{V_c}$, $(\frac{\partial V_d}{\partial x_c})_{V_d}$ equal to zero at a particular rotor speed. They are related to hold-up at flooding by equations:

$$V_{d(f)} = 2\bar{V}_N x_f^2 (1-x_f) \qquad (4.10)$$

$$V_{c(f)} = \bar{V}_N (1-x_f) (1-2x_f) \qquad (4.11)$$

The hold-up value at flooding is therefore:

$$x_f = \frac{(L^2 + 8L)^{0.5} - 3L}{4(1-L)} \qquad (4.12)$$

where $$L = \frac{V_{d(f)}}{V_{c(f)}}$$

This equation is inapplicable when the mean drop size is not constant over the entire hold-up region. In another study Reman (39, 45, 59,60) considered the effect of system variables on the limiting capacity. The effect of column geometry on capacity is as listed in Table 4.1. The capacity was found to decrease with increasing ratio of dispersed to continuous phase flowrates. The capacity data obtained was correlated by considering energy input/volume (N^3R^5/HD^2) as determining the drop size. A constriction factor C_R was introduced to allow for the effect of constrictions on settling of the drops. C_R was defined as the minimum of the three area ratios $(\frac{S}{D})^2$, $(1-(\frac{R}{D})^2)$ and $((\frac{S+R}{D})\sqrt{(\frac{S-R}{D})^2+(\frac{H}{D})^2})$

This correlation does not include the effect of physical properties although some properties, like interfacial tension, have a significant effect upon the drop size and settling rates.

Recently, with some systems, phase inversion has been found to occur at flowrates below flooding. Under such conditions phase inversion became the capacity limiting factor (57, 61-70).
There was an ambivalent region within which either phase could be dispersed. This was strongly dependent upon

the viscosity ratio of the phases, the interfacial tension and to a lesser extent on the rotor speed.

The Column Diameter

The diameter of the column is predictable by two different methods. The first approximate method is based on the physical properties of the system and can be applied when no experimental data is available. It requires estimation of the coalescence coefficient, Z, and velocity component, α, which are related to drop size. Therefore, the method involves trial and error. With most systems in the absence of mass transfer the extent of interdrop coalescence is apparently small.

The second method involves the determination of diameter based on scale up of pilot plant data on the assumption that the limiting flowrates are proportional to the power input per unit mass. Power input/mass is defined as:

$$E = \frac{4}{\pi} C_2 \frac{N^3R^5}{HD^2} \qquad (4.13)$$

where C_2 is the coefficient in the power number

$$C_2 = \frac{P}{n\rho N^3R^5} = \qquad (4.14)$$

For a given system N^3R^5/HD^2 is an important variable determining the drop diameter and consequently the limiting volumetric flowrates.

The Column Height

The total column height is the sum of the height of the coalescence section, the height of the disperser section and the height of the extract column section itself. The height of the coalescence section depends upon the droplet flocculation and coalescence time and dispersed phase flowrate. For some systems with slow rates of separation (e.g. low σ and low $\Delta\rho$) and which therefore require high column sections, it is preferable to provide an external settler. At the opposite end of the column it is necessary to allow sufficient height for disentrainment of the dispersed drops from the out-flowing continuous phase. The height of this section depends on the size and velocity of the drops. The effective extractor height is determined by the usual concept:

$$h_{eff.} = HTU \times NTU \qquad (4.15)$$

where for the raffinate phase HTU and NTU are;

$$HTU = \frac{Vd}{k_d A} \qquad (4.16)$$

$$NTU = \ln \frac{\left(\frac{x_{R1} - x_{E2}/m}{x_{R2} - x_{E2}/m}\right)\left(1-\frac{1}{\xi}\right) + \frac{1}{\xi}}{1 - \frac{1}{\xi}} \qquad (4.17)$$

This method suffers from the limitation that the HTU varies with rotor speed and axial mixing. Also the efficiency is affected by the geometrical parameters of the column (45,71).

In a recent study (58) mass transfer was expressed by the following relationship based on the assumption that total mass transfer comprised the net effect of a large number of oscillations and complete cycles of formation and coalescence.

$$\sum_{n=1}^{n}\left[\sum_{i=1}^{i}\int\left[\frac{dx}{x-x^*}\right]_i\right]_n = \sum_{n=1}^{n}\left[\sum_{i=1}^{i} A_i/V_i \int k_i\, dt\right]_n \qquad (4.18)$$

where i refers to any particular phenomenon, drop formation, drop oscillation etc. and n is the compartment number. However, this model relies on single drop correlations and has not been extended to multidrop systems. Also, like other relationships, it cannot be used with confidence since axial mixing has a considerable effect on mass transfer efficiency, but no allowance is made for this. The effect of axial mixing on efficiency is briefly discussed in the following section.

4.3. Mass Transfer Efficiency and Interfacial Phenomena

Prediction of mass transfer efficiencies of extraction columns without consideration of the effect of longitudinal mixing has resulted in some unreliable correlations (72,73,74, 75). Longitudinal mixing has an undesirable influence on the efficiency because it decreases the driving force for mass transfer due to concentration jumps occurring at the phase inlets and outlets. Several models have been proposed to describe mass transfer with axial mixing; i.e. the stage model(76), the backflow model

(77, 79, 79), the diffusion model (77, 78,79,80,81,82,83) and the combined model (43, 84).

4.3.1. Axial Mixing in RDC and Mass Transfer Efficiency

In order to characterise axial mixing in the RDC, it is first necessary to determine the eddy diffusion and back mixing characteristics. The axial mixing coefficient includes the effects of eddy diffusion as well as the spreading effect specifically in the forward direction. The axial mixing coefficient is then used to correct the calculated column efficiency for the effects of axial mixing.

As an aid in developing an axial mixing correlation for a single phase flow, resistance measurements were made in an electrical conductivity cell-analogue of an RDC by using dimensionless conductances as;

$$\left(\frac{S}{D}\right)^2,\ 1-\left(\frac{R}{D}\right)^2,\ \left(\frac{S}{D}\right)^2-\left(\frac{R}{D}\right)^2,\ \left(\frac{H}{D}\right)\left(\frac{S+R}{D}\right)$$

The axial mixing coefficient was then correlated to these (54) parameters as:

$$\frac{E_a}{\nabla_N H} = 0.5 + 0.09\left(\frac{RN}{\nabla_N}\right)\left(\frac{R}{D}\right)^2\left(\left(\frac{S}{D}\right)^2-\left(\frac{R}{D}\right)^2\right) \qquad (4.19)$$

for $\frac{RN}{V_N} > 30$

and with dispersed phase flow;

$$\frac{(1-x_d)\ E_c}{V_c\ H} = 0.5 + 0.09\ (1-x_d)\left(\frac{RN}{V_c}\right)\left(\frac{R}{D}\right)^2\left(\left(\frac{S}{D}\right)^2-\left(\frac{R}{D}\right)^2\right) \qquad (4.20)$$

For dispersed phase axial mixing this equation becomes;

$$\frac{x_d E_d}{V_d H} = 0.5 + 0.09\, x_d \left(\frac{RN}{V_d}\right)\left(\frac{R}{D}\right)^2\left(\left(\frac{S}{D}\right)^2 - \left(\frac{R}{D}\right)^2\right) \qquad (4.21)$$

This equation is applicable to the RDC at high rotor speeds as under these conditions the eddy diffusion dominates the axial mixing process. However, axial mixing studies need to be related to drop size distribution.

For a countercurrent device the eddy diffusion mass transfer model has been developed by using the plug flow equation to calculate the efficiency. By this approach the Peclet number is related to axial mixing coefficient when the feed is the dispersed phase as:

$$N_{Pe_f} = \frac{V_d H}{x_d E_a} \cdot \frac{L}{H} \qquad (4.22)$$

$$N_{Pe_s} = \frac{V_c H}{(1-x_d) E_a} \cdot \frac{L}{H} \qquad (4.23)$$

and when the solvent phase is the dispersed phase by;

$$N_{pe_f} = \frac{V_c H}{(1-x_d) E_a} \cdot \frac{L}{H} \qquad (4.24)$$

$$N_{Pe_s} = \frac{V_d H}{x_d E_a} \cdot \frac{L}{H} \qquad (4.25)$$

The axial mixing diffusivities given in equations 4.18 and 4.19 can be used as the eddy diffusivities. The expression for Number of Transfer Units for plug flow

condition is given by:

$$\frac{NTU}{NTU_p} \quad \frac{N_{Pe_f}\, N_{Pe_s}}{N_{Pe_f}\, N_{Pe_s} - NTU_p\,(aN_{Pe_f} + bN_{Pe_s} + \sqrt{N_{Pe_f} N_{Pe_s}} - \sqrt{N_{Pe_f} + N_{Pe_s}} + f(N_{Pe_f} - N_{Pe_s})\, e^{-gNTU}} \qquad (4.26)$$

The coefficients a, b, c, d, e, f and g in the above equation are given in a tabulated form as function of extraction factor F. NTU_p can be calculated from the plug flow equation for mass transfer by:

$$NTU_p = \frac{1}{F-1} \ln \frac{1-\psi_p}{1-F\psi_p} \qquad (4.27)$$

NTU must then be determined by trial and error since it also appears in the term $e^{(-g\ NTU)}$ in equation (4.26).

4.3.2. Droplet Behaviour

The mass transfer rate depends upon the drop size and the hold-up of the dispersed phase since these determine A in equation 4.1. The calculation of hold-up was briefly described in section 4.2. The mode of mass transfer is also dependent on the drop size.

The size of the drops formed by flow through a non-wetted perforated plate is related to the physical properties of the system and nozzle diameter by (85):

$$\frac{\pi d}{6} + 4.11\times10^{-4}\ \frac{\pi d}{6}\ \frac{(\rho_d V)}{\Delta\rho} = 21\times\ 10^{-4} \left(\frac{\sigma d_n}{\Delta\rho}\right) + 1.069\times10^{-4}\ (d_n^{0.747}\ V^{0.355}\ \mu c^{0.186})^{3/2} \qquad (4.28)$$

However, if the dispersion is formed mechanically without the use of a disperser, the prediction of the drop size is based on the energy distribution law (86,87).

$$d_m = C_1 \left(\frac{g_c \sigma}{\rho_c} \right)^{3/5} E^{-2/5} \qquad (4.29)$$

This equation for maximum drop size is based on the assumption of an isotropic homogeneous turbulence and where the micro scale turbulence is smaller than the drop size. E is the power mass ratio and is related to the dimensions of the equipment by the relationship;

$$E = \frac{4\ P}{\pi D^2 \rho_c\ N\ H} \qquad (4.30)$$

The constant C_1 is predicted as 0.72 (88). Equations of similar form have been used by other workers to estimate the maximum drop size (53,89).

The following expression was derived to predict the drop size in an RDC within the turbulent mixing region (90).

$$\frac{d_o\ N^2\ D\ \rho_c}{\sigma\ e^{0.0887_{\Delta D}}} = 16.3 \left(\frac{H}{D}\right)^{0.46} \qquad (4.31)$$

where ΔD is the distance of impeller from wall.

The assumptions were:

i. Splitting of drops occurs under conditions when the magnitude of the dynamic pressure, acting upon the

drop, surpasses the magnitude of the cohesive surface forces of the drop.

ii. The highest dynamic pressure acts upon the liquid near the column wall and is proportional to the square of the continuous phase velocity at this location.

iii. The velocity of the continuous phase in the vicinity of the impeller is proportional to its peripheral speed and diminishes exponentially towards the column wall.

iv. The vertical velocities of both the dispersed and continuous phases have a negligible effect on the splitting of drops.

v. The influence of compartment height may be expressed by a simple exponential function of $\frac{H}{D}$.

However, the above equations do not consider the equilibrium drop size arising from the competing effects of coalescence and the break-up of the drops. These factors would greatly change the interfacial area calculated from this drop size.

It has been found experimentally (54) that if E in equation (4.29) is less than 1.0 the mean drop size is 0.7 times the maximum drop size calculated from equation (4.28).

$$d = 0.7\, d_m \qquad (4.32)$$

Mass transfer to and from drops has been studied extensively and the efficiencies of mass transfer estimated for different stages of the drop life i.e., during formation, during release, during travel through the continuous phase and during coalescence.

Mass Transfer During Drop Formation

During drop formation the surface area is estimated from the volume of the drop as a function of the time of formation. The relationship between the volume of the drop and the time of formation has been studied for four different regions. Correlations have been developed for each region giving volume as a function of the physical properties of the system (12,13,54,91-93). The surface area-volume relationship was predicted experimentally for several systems and a linear relationship was obtained.

The theory of diffusion was applied to calculate the mass transfer efficiency using the equation:

$$E_f = F \left(\frac{Dtf}{\pi}\right)^{\frac{1}{2}} \qquad (4.33)$$

Four models were recommended for the estimation of mass transfer efficiency. All these models were based on the above equation. The assumptions were:

(i) The interfacial concentration is that at saturation.

(ii) Mass transfer by diffusion is perpendicular to the interface.

(iii) The process of diffusion is slow as compared with the process of drop growth.

(iv) Variations in the diffusion coefficient in the direction of flow are neglected.

However, it was found that these models were inaccurate as they did not consider the internal circulation and interfacial turbulence, or the influence of rest, time of a drop between formation and disturbances associated with the drop detachment (94).

The following empirical correlation was suggested (43) which included other parameters like density, viscosity and interfacial tension.

$$\frac{k_{df}\, t_f}{d} = 0.0432 \left(\frac{V_N^2}{dg}\right)^{0.089} \left(\frac{d^2}{t_f D_d}\right)^{-0.334} \left(\frac{u_d}{\sqrt{\rho_d\, \sigma\, d}}\right)^{-0.601} \qquad (4.34)$$

The average absolute deviation from data was 26%. This correlation represented the overall mass transfer occurring during drop formation including mass transfer during drop growth, during the detachment and the influence of the rest drop.

Mass Transfer During Droplet Release

During droplet release changes occurring at the

interface and an oscillation of the drop caused by release result in a different magnitude of mass transfer efficiency to that during drop formation. Several workers (14,15, 95-98) have described different mass transfer mechanisms so that the exact mode is uncertain.

Mass Transfer in the Dispersed Phase

Mass transfer efficiency within a drop depends upon the Reynolds number within it. The interfacial tension between the continuous and the dispersed phase (99) and the nature of the original interface (100) also have a significant effect on the efficiency of mass transfer. Therefore, efficiencies differ with different system properties.

Mass transfer within the drops is characterised for three different types of drop, namely: rigid, circulating and oscillating drops. Drops of very small diameter, usually below 1mm., or larger in the presence of surface active agents, behave as rigid drops and the solute concentration varies according to the expression (101):

$$E = 1.- \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp.\left(-n^2 \pi^2 \frac{D_D t}{a^2}\right) \qquad (4.35)$$

Internal circulation causes the liquid in the drop to mix and therefore a higher mass transfer

coefficient is obtained. The circulation is laminar if the Reynolds number is less than 1.0. A Reynolds number above 6.0 produces turbulent circulation. The analysis of mass transfer inside a circulating drop is explained by molecular diffusion. One correlation proposed is (102),

$$E = 1 - \frac{3}{8} \sum_{n=1}^{\infty} A\, n^2 \exp.\left(- \frac{\lambda n\, 16\, D_D t}{a^2}\right) \quad (4.36)$$

This equation is in general applied to regimes with Re<1. For the case of turbulent circulation, another expression was proposed based on a turbulent flow; due to random radial motion, superimposed upon a circulatory pattern(103).

$$E = 1 - 2 \sum_{n=1}^{\infty} A\, n^2 \exp.\left(- \frac{\lambda n\, U_t}{128\, (1+ \frac{\mu_d}{\mu_c})\, d}\right) \quad (4.37)$$

In general at low continuous phase viscosities, when the Reynolds number is above 200, the drops are oscillating. Low interfacial tension and a low dispersed phase viscosity also favour oscillation. The expression developed (104) for vigorously oscillating single drops takes into account the amplitude and frequency of the oscillations.

$$E = 1 - \exp.\left(- \frac{2\pi D_E}{V} \int_{t_o}^{t_f} \frac{1}{f_1(t)} \left(\left(\frac{3V}{4\pi(a_o + a_p|\sin wt|)^2}\right)^{\frac{2}{2\alpha}} \ln \frac{1+\alpha}{1-\alpha} + (a_o + a_p|\sin wt|)^2\right) dt \right) \qquad (4.38)$$

Mass Transfer in the Continuous Phase

Mass transfer in the continous phase has also been studied separately for the cases of rigid and non-rigid drops. For a rigid drop the mass transfer coefficient was correlated to Reynolds number and Schmidt number by,

$$Sh = A + CRe^{m} + Sc^{n} \qquad (4.39)$$

Similar correlations were obtained for non-rigid drops.

$$Sh = K\ (Re)^{\frac{1}{2}}(Sc)^{\frac{1}{2}} \qquad (4.40)$$

The proportionality constant K was found to be 1.13 (105). Later, however, the contribution of dropwake to the mass transfer was considered and the constant was modified to 0.6 (106). For oscillating drops (16, 107, 108) equation (4.39) was further modified by Treybal (1) for a swarm of drops as;

$$Sh = 0.725\ (Pe)^{0.57}(Sc)^{-0.15}(1-\Phi_d) \qquad (4.41)$$

In other work the mass transfer coefficient in the continuous phase has been related to densities and

viscosities and the mean diameter of drops. Interaction between drops in swarms and the effect of particle size distribution were also taken into account (109):

$$k_c = 0.371 \left(\frac{D\,(\rho_c - \rho_d)\,g}{2\mu_c + 3\mu_d}\left(\frac{1}{2}d_{32}\right)\right)^{\frac{1}{2}} \qquad (4.42)$$

Mass Transfer During Coalescence

The contribution made to mass transfer during the coalescence of a drop into an interface has been studied. An identical correlation to that for formation was developed (14, 98, 110),

$$k_{dc} = \left(\frac{D_d}{\pi t_f}\right)^{\frac{1}{2}} \qquad (4.43)$$

However, this was later criticised because the driving force for mass transfer was much less than that during formation. Another expression was therefore derived (94).

$$\frac{K_{dc}\,t_f}{d} = 0.1727\left(\frac{\mu_d}{\rho_d D_d}\right)^{-1.115}\left(\frac{\Delta\rho\; g\; d}{\sigma}\right)^{1.302}\left(\frac{v^2 t_f t}{D_d}\right)^{0.146} \qquad (4.44)$$

Generally in pure systems the coalescence takes place rapidly without allowing enough time for a significant degree of mass transfer. Nevertheless, because of oscillations occurring as a drop approaches the interface, the mass transfer increases temporarily

and this may be taken into account.

The Overall Mass Transfer Coefficient

The overall resistance to mass transfer is calculated as the sum of the resistances of the individual phases. The controlling coefficient can be predicted from the drop size. If the drop size is larger than 2mm., the drops will oscillate and the continuous phase coefficient will be controlling. Also, if the time taken for the concentration of the drops to change by 95% is short, of the order of 30 seconds, the extraction will be controlled by the continuous phase. This is the most common case.

4.3.3. Application of Droplet Models to Practical Extraction

In general application of single drop mass transfer models to industrial contactors is very difficult. This arises because of the complexity of the mass transfer and droplet coalescence-redispersion processes, both of which may change with location and solute concentration within the contactor. The contributions made to mass transfer during each of the four stages of a drop's life have been discussed and a different correlation described for each stage. In practice, however, it is impossible to allocate a time for each stage. Also, once discrete drops form at the distributor they do not necessarily travel throughout a column until they coalesce. Break-up, or inter-drop coalescence may take place.

Furthermore, the mechanism of mass transfer to or from the formed drops is not the same along the column. Following mass transfer during travel, the physical properties such as interfacial tension, density difference, or viscosity change as does the driving force, i.e. the concentration difference and indeed the drop size. Hence, the mass transfer rate to an individual drop does not remain the same.

The presence of impurities is another important factor influencing mass transfer. Most mass transfer correlations presented previously apply to pure systems, with a minimum of impurities under ideal conditions. These seldom exist in practice. Because of impurities, interfacial tension differs and coalescence may be hindered.

In practice, calculation of mass transfer to or from formed drops involves estimation of a mean drop size which remains the same throughout the effective column height.

5. Equilibrium Studies Using Liquid Ammonia

Extensive studies of the equilibrium relationships between hydrocarbons and liquid ammonia were first made by Kirk (30). More than 400 individual experiments were carried out successfully in an apparatus designed to operate over a temperature range of -40°C to 95°C and to withstand pressures up to 34 bars. Franklin (11) first pointed out that visibility of the charge was important. In view of the interesting solubility characteristics obtainable, Kirk (30) therefore preferred an apparatus facilitating visual observation. This was necessary since the hydrodynamic behaviour of ammonia with hydrocarbons was unknown. Since ammonia has an absolute pressure of 8.7 bars at 20°C it had to be handled in vacuum-jacketed glass containers at temperatures below -33°C at which the vapour pressure is 1. bar.

The apparatus used by Kirk comprised sealed glass tubes specially designed and constructed to withstand pressures up to 34 bar. Since high operating pressures would have been required to keep ammonia in liquid form at temperatures above -33°C, this limited the size of the charge that could be handled safely. However, excellent visibility was obtained and the experiments were completed successfully.

The equipment used in the present work was much simpler since its main purpose was to provide sufficient data for the equilibrium curve on the ternary diagram to be used in the extraction of aromatics in the RDC.

5.1. Description of Equipment

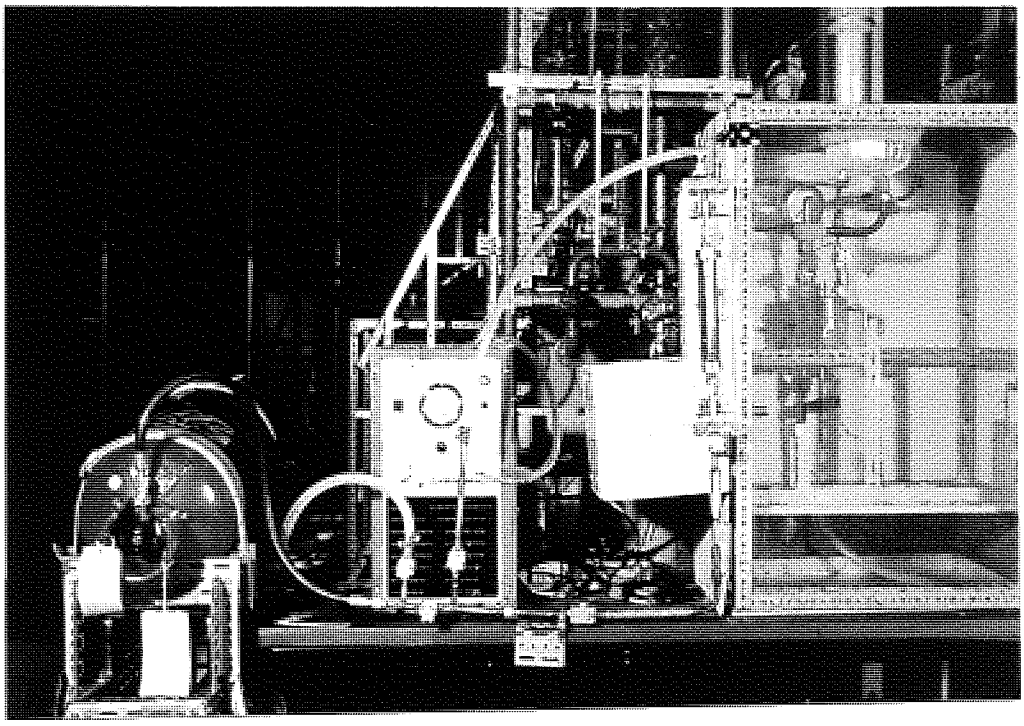
Phase equilibria of ternary systems in which one of the components was liquid ammonia were determined at high pressure in an equilibrium bomb of 1500 ml. capacity. This is illustrated in Figure 5.1 and the construction and dimensions are shown in Figure 5.2. The bomb was jacketed and cooling water at a constant temperature, from a thermocirculator, was circulated through the jacket at sufficient rate to maintain the temperature of the contents constant. A drain line, and vent and feed lines were provided at the bottom and top flanges respectively. These flanges were welded to both the inner tube and the outer shell of the bomb.

The bomb was tested hydraulically at 35 bar and in addition all the pipe joints were tested with nitrogen at 10.2 bars. A pressure relief valve was provided to release pressure if it exceeded 10.2 bars. Two sampling ports were provided, one fixed to the bottom flange and another on the side at 89 mm. from the bottom to enable samples to be drawn from the bomb by means of gas tight syringes. Use of the sampling ports did not in fact prove practicable because the valves of the gas tight syringes could not maintain a seal.

Liquid ammonia was supplied from a 29 kg. capacity cylinder supported on a specially designed framework at an angle of 5^{o} from the horizontal. The stainless steel ammonia feed line was 2.0 m. long and varied in diameter from 6 mm. to

Figure 5.1.

ARRANGEMENT OF EQUILIBRIUM BOMB



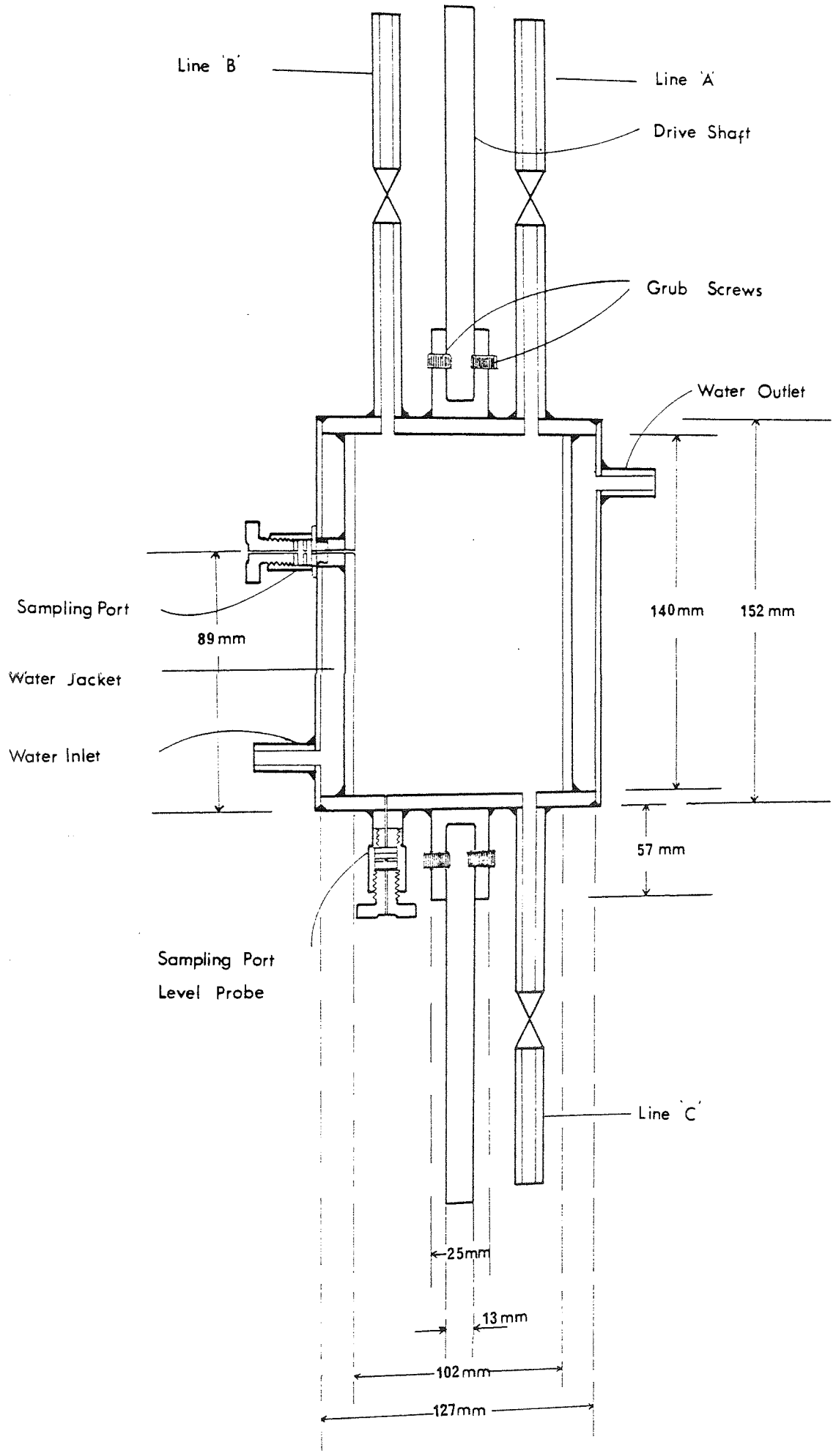
Operating Pressure = 8.8. Bar, (= 130 psi) approx.

Operating Temperature = Ambient.

29 kg, ammonia cylinder in position for liquid discharge. Constant temperature water supply apparatus on left of cabinet containing bomb. Bomb in vertical position for charging.

DETAILS OF EQUILIBRIUM BOMB

Operating Pressure : 10.2 bars Test Pressure : 35 bars



18 mm.; it had a total hold-up of 200 ml. A vent line was provided for venting off the ammonia left in the feed line after charging. A high pressure sight glass was fitted in this line so that the ammonia charge could be observed; this was essential to avoid pressurisation of the bomb by gaseous ammonia before liquid could enter. A non-return valve was provided to prevent back flow into the ammonia cylinder; this could otherwise have arisen since the solubilities of aromatic hydrocarbons in ammonia are fairly large. Nitrogen from a standard cylinder was used for the purposes of pressure testing the system and pressurising the bomb after ammonia had been charged.

A frame was constructed to support the bomb horizontally for mixing to attain equilibrium. The bomb was connected by 2 grub screws to the drive shaft of a 0.335 kW motor transmitting rapid reciprocating motion. A single stage "Speedivac" vacuum pump was provided to obtain vacuum before hydrocarbons charging and during sampling. The bomb and pipe lines were of stainless steel; p.t.f.e. and 'Stag' jointing compound were used to seal threaded joints. Compression couplings were used to connect the bomb to the feed line during charging and to the sampling pot during sampling. They were also used to fix the pressure gauge to line "B" (Figure 5.2.) while charging and on subsequent pressurisation with nitrogen.

The complete assembly was installed inside a ventilated cabinet as shown in Figure 5.1. This was provided with a

clear reinforced PVC door and was exhausted to outside the building via flexible ducting. All the vent lines were inserted inside this ducting.

The ancillary equipment provided is discussed in Section 6.

Operating Procedure

(Cumene-n-heptane-ammonia system)

Prior to charging the hydrocarbons, the bomb was washed with Decon solution; it was then drained and rinsed through with water. To remove any hydrocarbons which may have been retained from a previous experiment it was also rinsed with acetone. This was followed by drying with compressed air.

The bomb was positioned vertically on the metal frame, connected to the feed line and then purged with nitrogen to displace any air. It was next evacuated down to 25mm. Hg. pressure via valve VII. The piping arrangement during ammonia charging is shown in Figure 5.3. A hydrocarbon mixture of Cumene and n-Heptane, of known volumetric ratio, was fed into the bomb via line "B" using a tundish and without loss of vacuum. A pressure gauge was subsequently connected to this line with valve V9 shut. The compression coupling connecting the drain line to the vacuum pump was broken and the line was capped. To allow all non-condensibles and air to be purged from the charge line, valve V8 was cracked open. Keeping V1 and V3 shut; with V2, V4, V5, V6

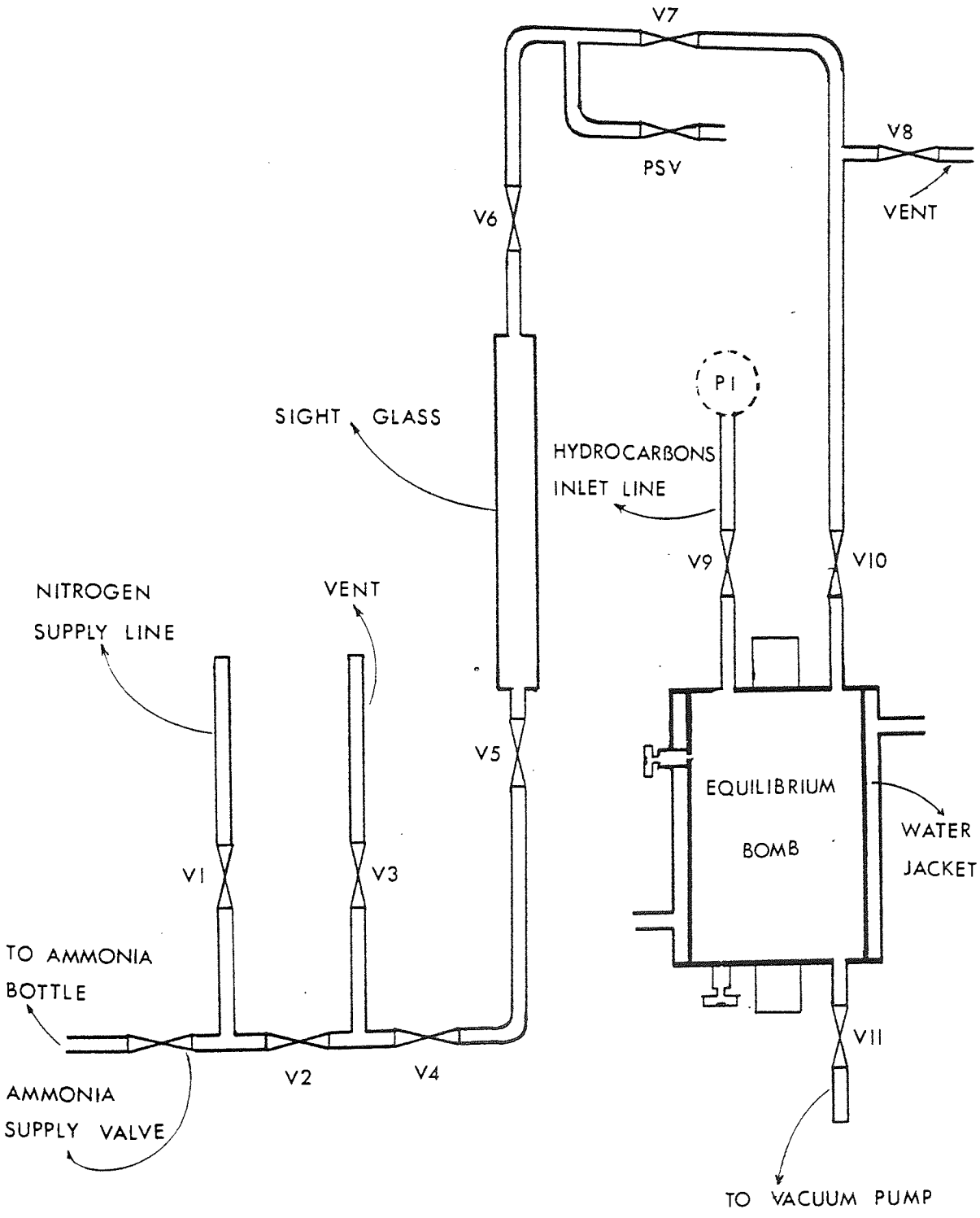


Figure 5.3

PIPING ARRANGEMENT ON EQUILIBRIUM BOMB

DURING AMMONIA CHARGING

V7 open the ammonia supply valve was then cracked open. Liquid ammonia was evaporated under controlled conditions, with gas venting to atmosphere, until liquid appeared in the sight glass. V8 was then closed and V10, the inlet to the bomb, opened. Increasing pressure was monitored on the pressure gauge. The amount of ammonia flowing into the bomb could not be measured, although this was attempted with a rotameter and a timer. Liquid ammonia flowed by pressure difference and as the pressure built up in the bomb the flow rate gradually decreased; when the pressure in the ammonia cylinder equalised that in the bomb the flow stopped. To force more ammonia into the bomb gaseous ammonia had to be vented from it by closing valve V7 and cracking open valve V8. The pressure in the bomb could be reduced down to 6.1 bars. in this way, so that further liquid ammonia could be fed into the bomb by pressure difference. Initially, since liquid ammonia was flashed off, the bomb was cooled. However, as the temperature reached a steady value the ammonia in the mixture tended to boil and hence provide a source of gas, thereby causing an increase in pressure. To prevent this boiling at room temperature the bomb was pressurised to 10.2 bars. with nitrogen above the saturation pressure at room temperature. This technique also helped to standardise the amount of liquid ammonia charged.

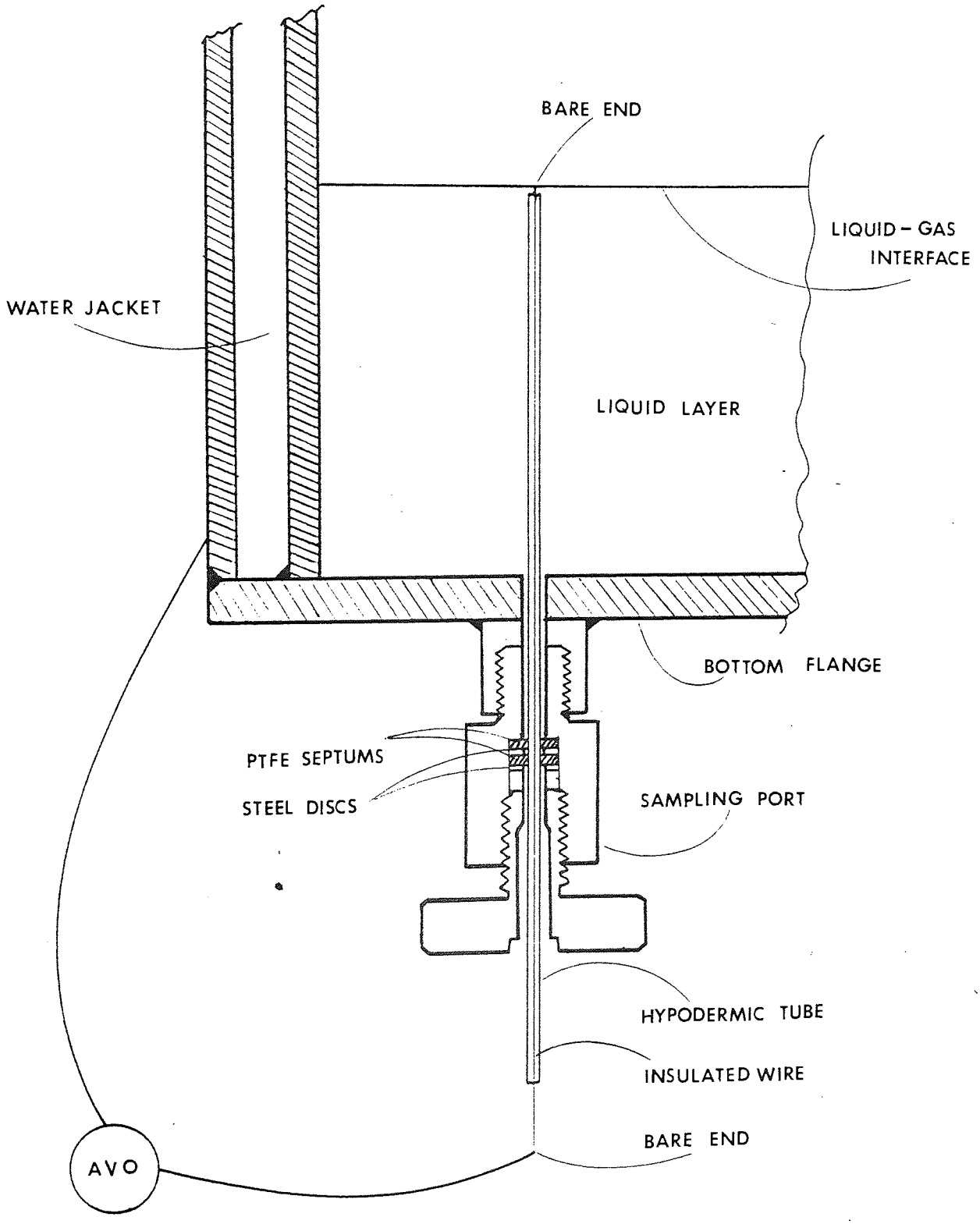
As mentioned earlier, it was impossible to determine the amount of ammonia charged to the bomb because anhydrous liquid ammonia taken straight from the cylinder initially

contained bubbles of gaseous ammonia which caused the rotameter float to fluctuate over a very wide range. Also since flow was maintained by a pressure difference, as the pressure in the bomb increased the flow decreased. Therefore, a conductivity circuit was used to locate the interface between liquid and gas in the bomb as shown in Figure 5.4. A fine insulated wire of known length passing through a hypodermic tube was used to complete a circuit between the liquid in the bomb and the case of the bomb. The insulation was removed at both ends of the insulated fine wire. The hypodermic tube was inserted into the bomb through the bottom sampling port. Since the electrical conductivity of the liquid phase was high compared with the gas, the depth of the liquid was found by means of an AVO multi meter connected between one end of the insulated wire and the bomb. From the total volume of liquid in the bomb and knowledge of the initial hydrocarbons volume, the amount of ammonia could then be calculated. Therefore, the feed point on the triangular diagram was determined.

The bomb was attached to a clamp arranged horizontally as in Figure 5.5., and the mixture was agitated by the motor. Before mixing all the outlet lines were capped to guard against the valves leaking. In order to ensure equilibrium, mixing was maintained for 24 hours. This was followed by a 2 hour settling period with the bomb positioned vertically for the two phases to separate. Two hours settling was found sufficient to obtain consistent compositions of representative

Figure 5.4

ARRANGEMENT FOR LOCATION OF THE INTERFACE BETWEEN LIQUID AND GAS BY MEANS OF AN AVO METER



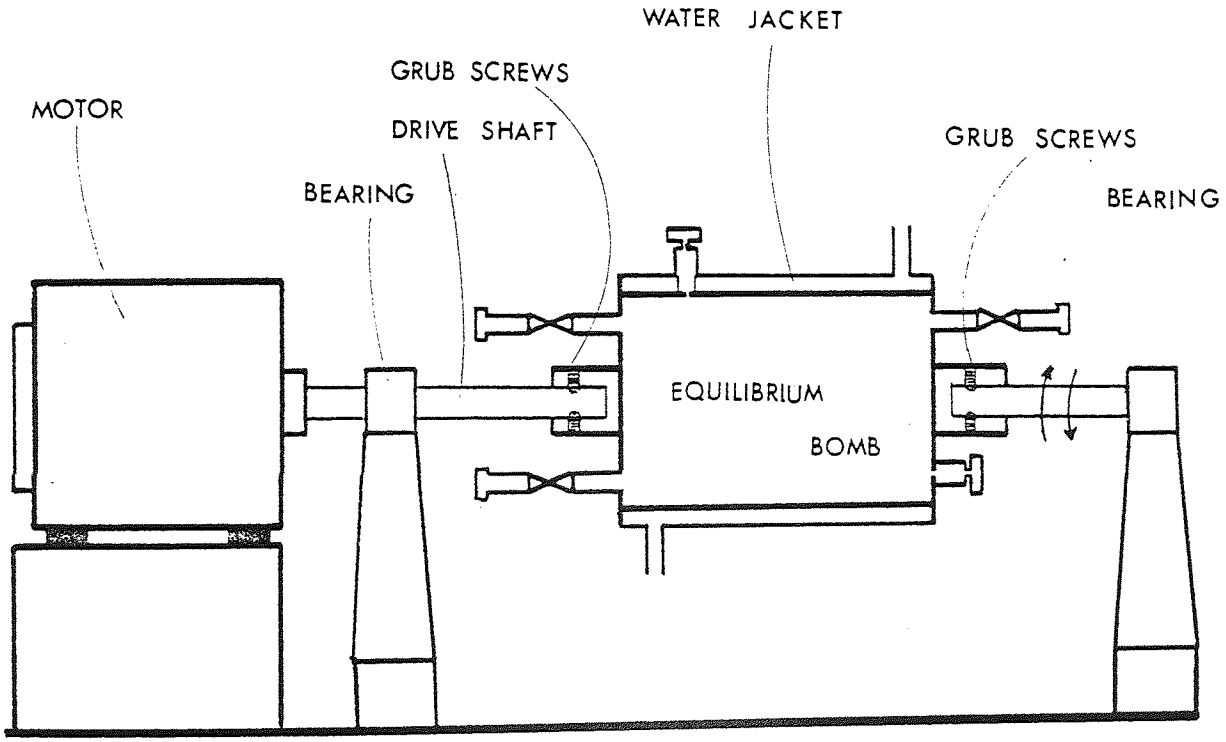


Figure 5.5

EQUILIBRIUM BOMB ARRANGEMENT FOR MIXING

samples from both layers.

5.2. Sampling and Analysis

Equilibrium studies at relatively high pressure introduce complications in sampling and analysis of the samples. Kirk (30) analysed samples taken from both heavy and light phases by determination of the amount and the composition of solvent and the amount and the composition of the solute in the phases. The easiest way to analyse the solvent, or modified solvent, was by titration with a standard acid, such as sulphuric acid with methyl orange as the indicator. Subsequently, in a study by Braun (34) the analyses of the products were made by fractional distillation and silica gel adsorption. The raffinate and extract recovery units consisted of packed columns of 76 mm. diameter and 6.40 m. high and 152 mm. diameter and 3.05 m. high respectively. Both columns were packed with Rachig rings and operated at atmospheric pressure. These columns eliminated the solvent from the products leaving only hydrocarbons to be analysed. The analysis of the hydrocarbons was carried out in a silica gel adsorption column. Ethyl alcohol was used as desorbent. The adsorption columns used were 1 cm. in diameter glass tubes with a packed height of 2.44 m. The components were released in the following order: saturates or paraffins and naphthenes,aromatics and finally the alcohol. The small fractions collected from the column were identified by means of their refractive indices or Bromine numbers. The volume of each type of hydrocarbon

was then calculated. The amount and the composition of ammonia, i.e. solvent, in the products were not found analytically.

In the present work the solvent recovery system was entirely different. Since it was a semi-continuous extraction process other methods had to be developed for intermittent sampling. A special technique had to be developed in order to obtain samples without loss of any of the components. Drawing liquid samples at high pressures using gas tight syringes proved impossible; the gas tight valves leaked persistently and allowed ammonia to evaporate before the sample could be injected into the chromatographic column. Analysis by mass spectrometry was found impracticable due to the absence of a differential pressure for charging samples.

The method developed for analysis of the phases involved first agitating the contents of the bomb with carbon-tetrachloride to dissolve the cumene and heptane and dilute acid to dissolve the ammonia.

Known quantities of carbon tetrachloride and dilute sulphuric acid were initially placed in a 2.1 litre capacity sampling bottle. The bottle with 10. ml. of carbon tetra chloride and either 100 ml. or 500 ml. of normal sulphuric acid, depending on whether the sample was from an ammonia lean or an ammonia rich phase, was connected to the bomb as shown in Figure 5.6. To avoid excessive pressure build up in the bottle as liquid ammonia evaporated, the bottle was

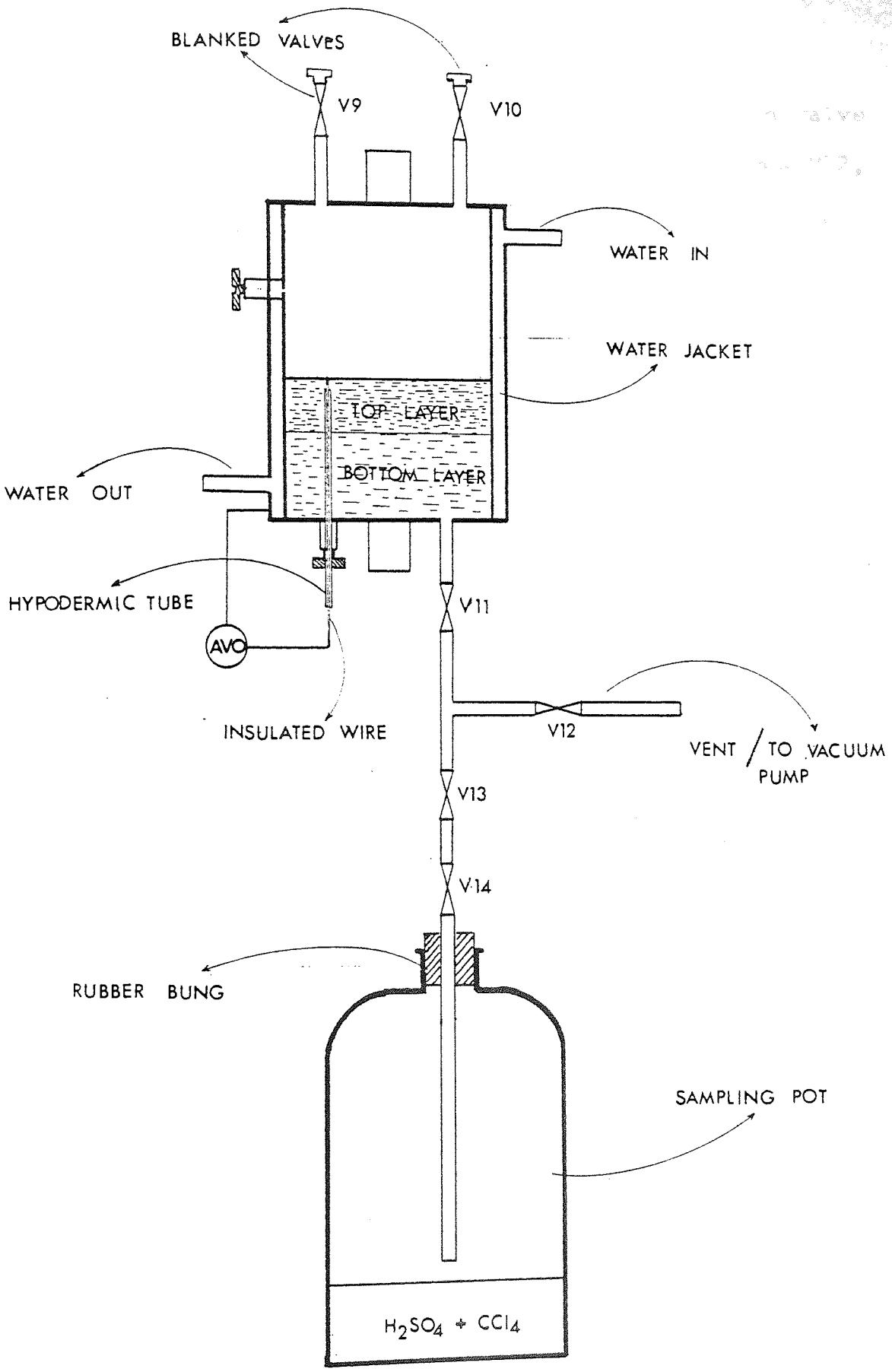


Figure 5.6

ARRANGEMENT OF EQUILIBRIUM BOMB FOR SAMPLE WITHDRAWAL

first evacuated down to 25 mm. Hg. During evacuation valve V11 was kept shut and V12, V13, V14 were open. Valves V12, V13, V14 were then shut and V11 was opened to let the sample fill the pipe line between V11, V12 and V13. V11 was then closed. To limit the pressure in the bottle the sample was introduced in small quantities. For this purpose V13 was opened and the sample was allowed to fill the small gap between V13 and V14. The sample trapped here was allowed to enter the sample bottle by cracking open V14. The valve was then closed and the bottle shaken vigorously until the cloudy gaseous layer on top of the liquid disappeared, i.e. until all the ammonia had reacted with sulphuric acid in the bottle. Simultaneously, the hydrocarbons dissolved in the carbon tetrachloride. This operation was repeated 10 to 15 times until all the sample had been collected. This was equivalent to 3 to 4 collections between V13 and V14. Before removing the bottle from the bomb the vacuum was broken by admission of air via V12 with V13 and V14 open.

5.3. Analysis of Samples

Following the procedure outlined above 3 to 4 representative samples were drawn from both bottom and top layers. Each sample was about 12 to 15 ml. After 3 to 4 samples had been drawn from the bottom layer the remainder was drained off until the top layer appeared. To drain the bottom layer the liquid collected between V11, V12, V13 was vented via V12 with V11, V13 closed securely. This was

continued until the ammonia-rich layer observed in the flexible PVC tube. Finally, 3 to 4 samples were taken from the top layer by a similar procedure and the residue in the bomb was vented and drained.

Different techniques were applied to analyse the acid-sulphate solution and hydrocarbons in the bottle. The sulphuric acid and ammonium sulphate mixture was titrated against 0.5 N sodium hydroxide solution using methyl orange as indicator to estimate the excess sulphuric acid. The amount which had reacted with ammonia was calculated by difference. Then, from a mass balance, the ammonia content of the sample was determined in terms of volume as the density at room temperature, i.e. 0.611 gr/cm^3 at 20^{o}C, was known.

The hydrocarbon mixture was analysed by chromatography. A Squclane column was used. This was programmed for temperatures between 80^{o}C and 100^{o}C. The first two peaks were carbontetrachloride and heptane with retention times of 2 and 8 minutes respectively at 80^{o}C. The temperature was then increased to 100^{o}C and the cumene gave a peak at relatively high retention time of about 24 minutes. The integrator values were converted to volume percentages for each of the three compounds using specific calibration charts determined in a separate set of experiments as described in Appendix 1A. Since the total volume ofcarbon tetrachloride was known, volumes of cumene and heptane could also be determined hence the volume percentages of each of the three components in the

samples could be calculated, and positioned on the triangular diagram as ends of the tie line passing through that particular feed point.

5.4. Results and Discussion of Results

For each determination, samples were taken from both the top and bottom layers and analysed. The results for samples representing the same top or bottom layer of a particular feed composition were generally reproducible within an accuracy of 1. to 2.%. This was considered satisfactory because, FID system was rather insensitive with small amounts, i.e. below 10% of heptane and cumene in 10 ml. of carbon-tetrachloride. This resulted in inaccuracies mostly for the points situated at the ammonia-rich corner of the triangular diagram. The curves produced to relate the integrator values to volume percentages were used for the three components; a correction was made by totalling the percentages to 100, and the corrected volume for each component was then found. An example of the method is given in Appendix 1B. Standard solutions of sulphuric acid and sodium hydroxide were used throughout and, since before titrating a cross-check was made using the standard acid and standard hydroxide solutions, the error introduced in titration was negligible compared with that in the chromatographic analyses.

Several problems occurred during sampling causing loss of some samples or necessitating repetition of the

experiment. In initial experiments analyses of samples representing the same product were inconsistent because the time allowed for settling was insufficient and the bottom layer was contaminated with the dispersed top layer. The necessary settling time of 2 to 3 hours was determined by trial and error and the experiments repeated.

Another practical problem during sampling was leakage past the valves. The valves were standard ¼" PTFE diaphragm valves and the diaphragms ruptured after a short while in service, possibly as a result of consecutive vacuum and pressure application and frequent use.

In the first two experiments listed as 1S and 2S in Appendix 1C the tie lines determined experimentally do not pass from the feed points M1 and M2. The only explanation for this is that, as mentioned above limited accuracy was obtained with the FID system, at very low percentages of Heptane and Cumene in 10 cc of carbon tetrachloride.

The equilibrium curve obtained from these experiments is shown in Figure 5.7. and a list of results, with a worked example are shown in Appendix 1D . To check consistency of the data and to aid interpolation the Othmer-Tobias Method was applied with coordinates $\frac{1 - X_{AA}}{X_{AA}}$ and $\frac{1 - X_{BB}}{X_{BB}}$ where X_{AA} and X_{BB} are the mole fractions of heptane in the heptane-rich-layer and ammonia in the ammonia-rich layer respectively. A straight line was obtained confirming the tie lines shown in

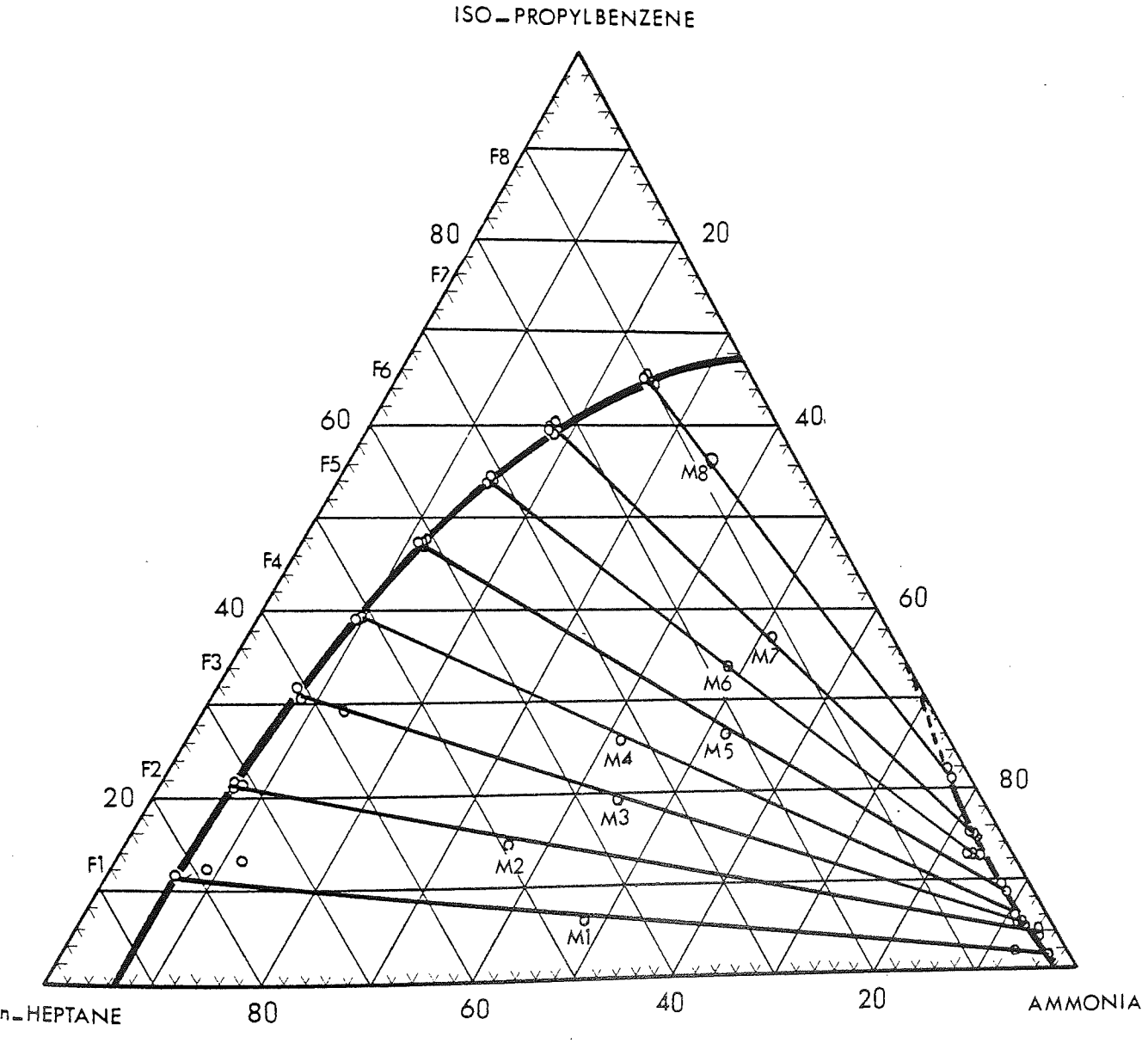


Figure 5.7

EQUILIBRIUM RELATIONSHIP OBTAINED FOR TERNARY SYSTEM

AMMONIA-ISO-PROPYLBENZENE-n-HEPTANE

AT 150 psi PRESSURE AND AMBIENT TEMPERATURE

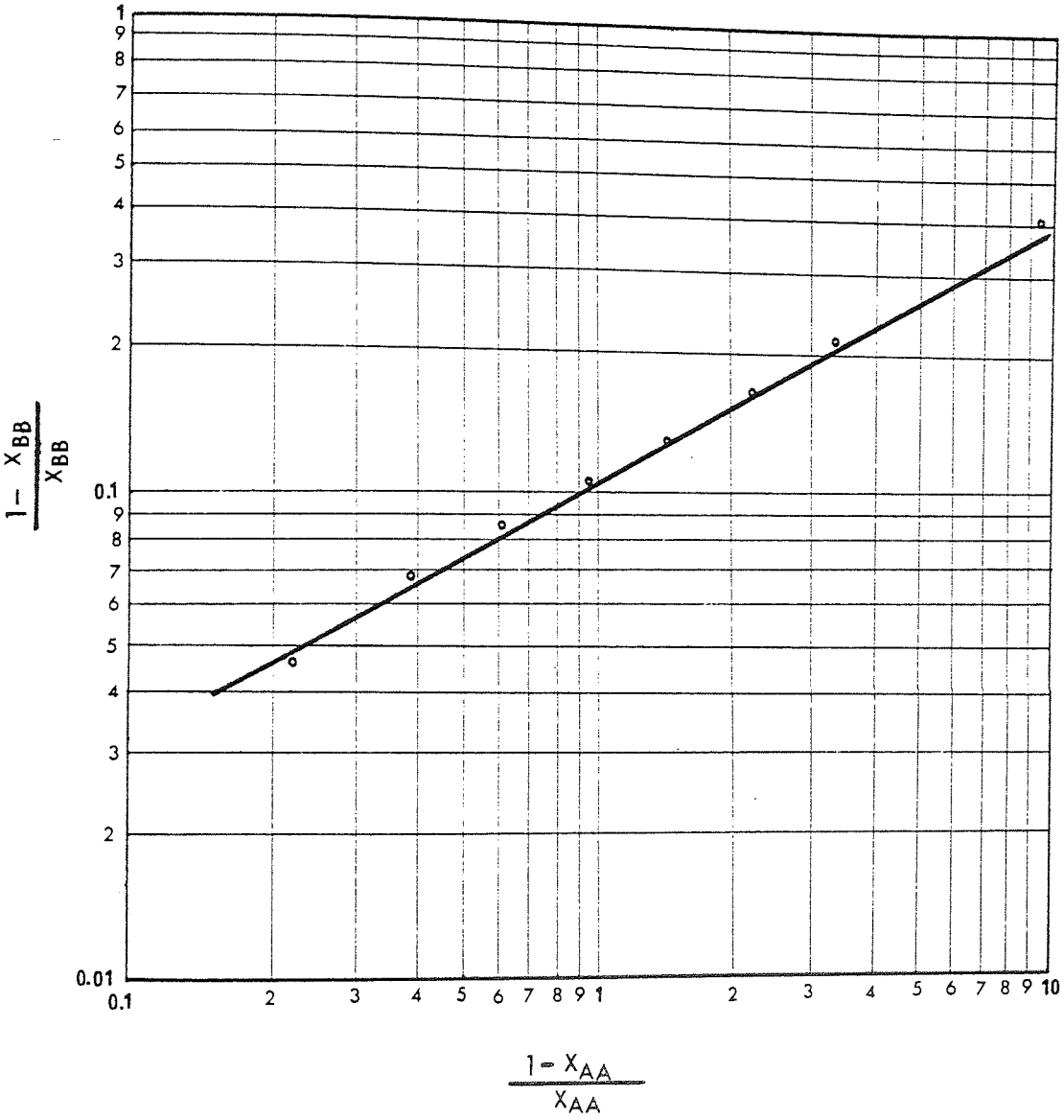


Figure 5.8

RESULTS OBTAINED TABULATED ON

OTHMER-TOBIAS

COORDINATES

Figure 5.7. The Othmer-Tobias diagram is shown in Figure 5.8.

Early results indicated that the equilibria were relatively insensitive to temperature changes of the order of $0^{o}C$ to $5^{o}C$. Therefore, the water jacket was not used and all the results determined at room temperature, i.e. between $17^{o}C$ to $20^{o}C$. Since the data was required only for interpretation of extraction experiments performed at ambient temperature in the pilot plant, the facility provided to maintain constant temperature in the equilibrium bomb was not used.

6. Experimental Investigation

6.1. Equipment

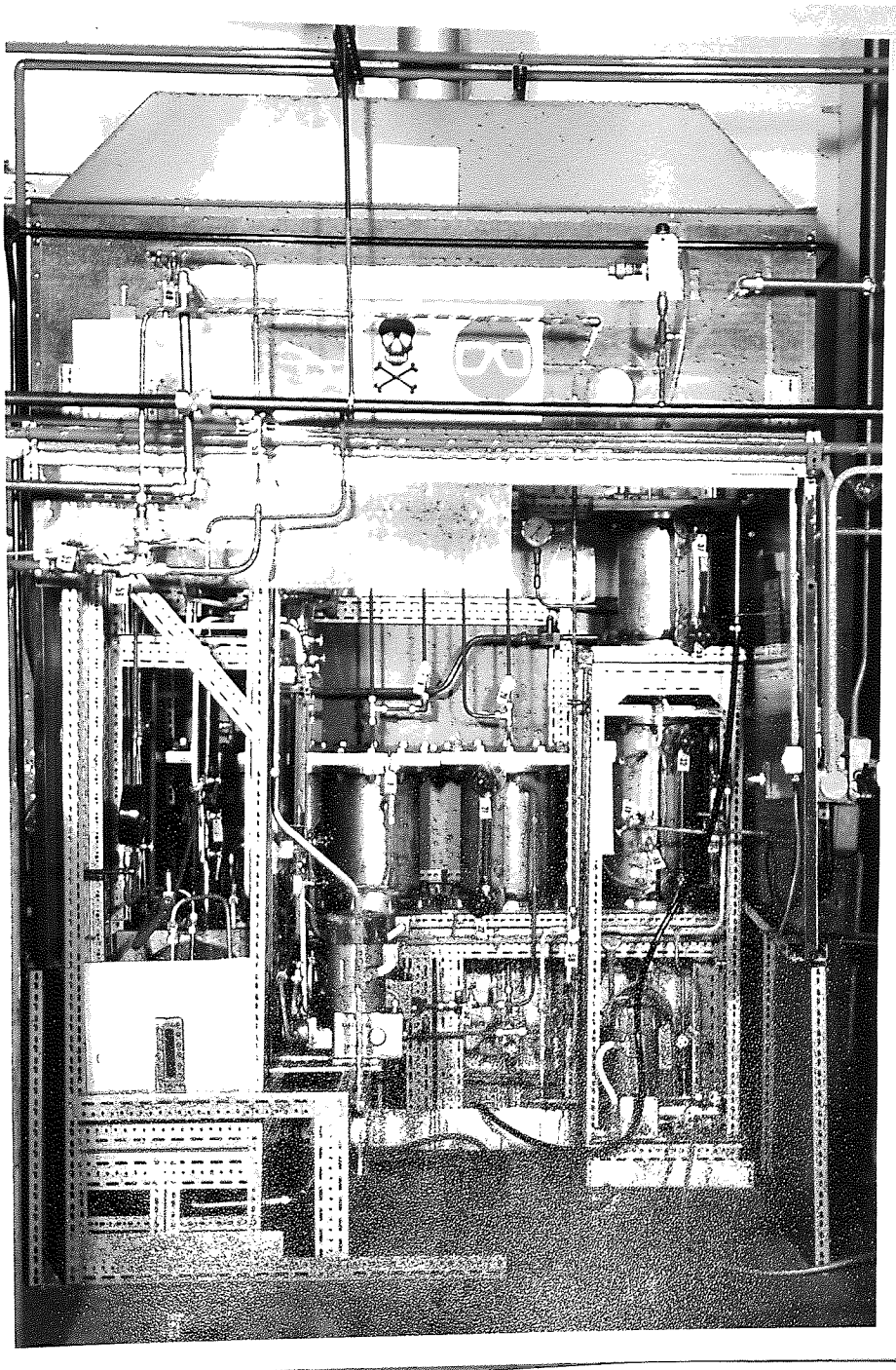
The advantages of ammonia as a solvent for the separation of aromatics from non-aromatic hydrocarbon mixtures were described in Section 3. Pilot scale equipment was designed and constructed to investigate its use with two typical systems. The equipment is shown in Figure 6.1. It incorporated an R.D.C. of 5cm. internal diameter, two settler vessels, five storage vessels, and a complete solvent recovery unit.

Due to the low boiling point of ammonia (-33°C) the operating pressure at ambient temperature must always be maintained above the vapour pressure at ambient temperature . 9.0 to 11.0 bar pressure was therefore selected as the operating pressure in this case.

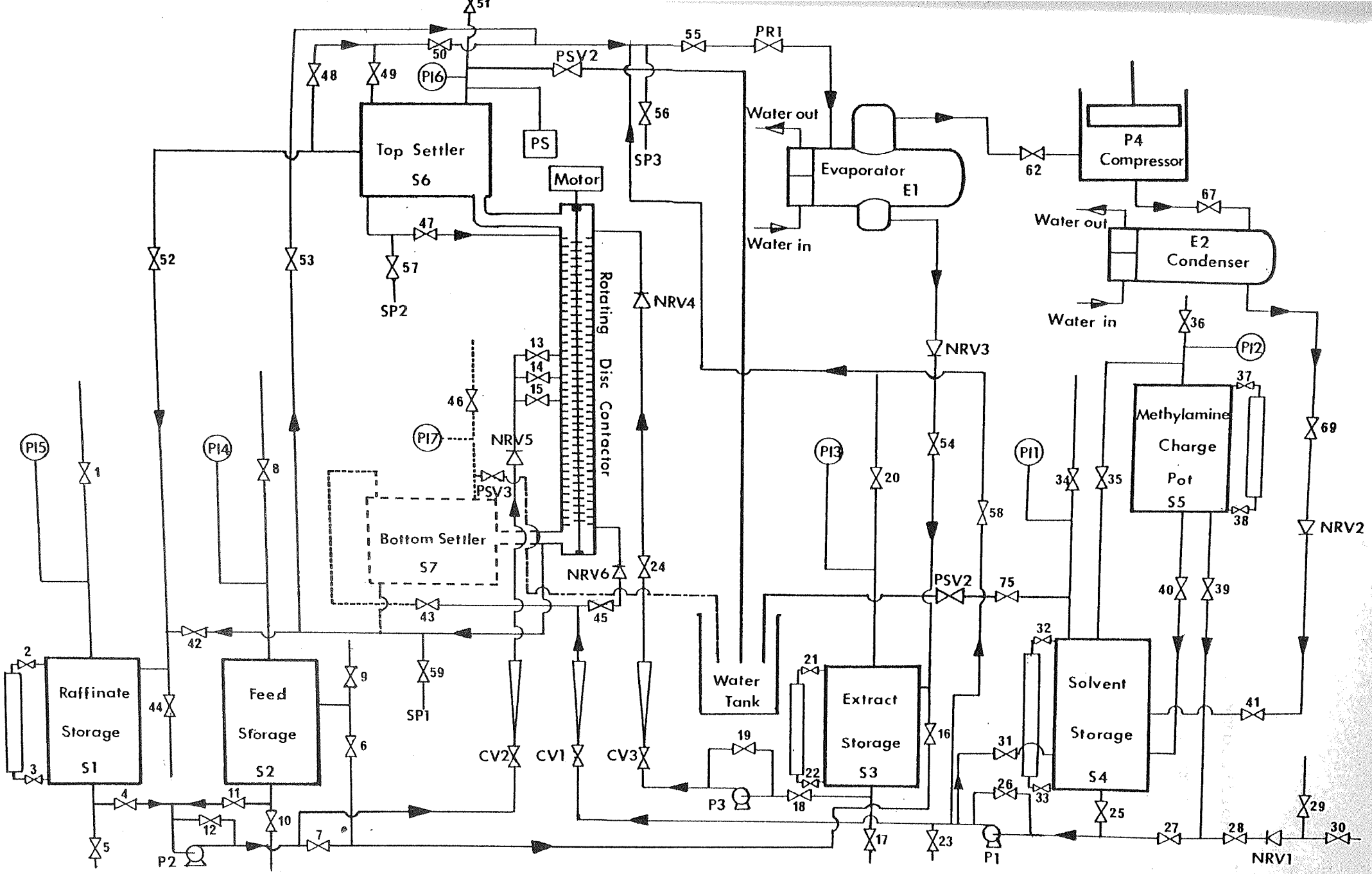
The feedstock comprised a mixture of an aromatic and a non-aromatic hydrocarbon. In selecting this mixture it was necessary to consider the freezing point, boiling point, flash point, toxicity characteristics and solubility in ammonia of the constituents and their cost. Systems N-heptane - Iso-propyl benzene (Cumene) - Ammonia and, Methylcyclohexane-Toluene-Ammonia were selected from a number of suggested hydrocarbons listed in Appendix 2 . For the system N-heptane-Cumene-Ammonia the equilibrium data were established experimentally as described in Section 5. Equilibrium relationship for the system Methylcyclohexane-Toluene-Ammonia was obtained from the

Figure 6.1.

LIQUID-LIQUID EXTRACTION PLANT USING LIQUID AMMONIA AS SOLVENT



5cm. internal diameter RDC left background
Storage vessels S2, S3, S4, S5 on the right side with pumps beneath
Equipment enclosed with extraction canopy over and sliding access door.
(Solvent recovery unit not shown).


Top Settler
S6
Bottom Settler
S7
Rotating Disc Contactor
Motor
PS
PSV2
PSV3
PR1
PI1
PI2
PI3
PI4
PI5
PI6
PI7
NRV1
NRV2
NRV3
NRV4
NRV5
NRV6
SP1
SP2
SP3
Evaporator
E1
Water out
Water in
P4
Compressor
E2
Condenser
Methylamine
Charge
Pot
S5
Water
Tank
Extract
Storage
S3
Solvent
Storage
S4
Raffinate
Storage
S1
Feed
Sforage
S2
CV1
CV2
CV3
P1
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literature (35). Mixtures of predetermined composition were fed to the R.D.C. for the extraction of the aromatic component Cumene or Toluene.

The complete flowsheet of the plant is shown in Figure 6.2. The R.D.C. comprised a 5cm. internal diameter, 125cm. long steel column containing 50 compartments. Storage vessels S1, S2, S3 and S4 were provided for the storage of the feed, the raffinate, and extract phases and the solvent. An additional vessel was provided for storage of a modifying agent for the solvent; this was selected as either mono-methylamine as a prosolvent, or water as antisolvent, depending upon the solubility characteristics of the system.

Ammonia was stored in vessel S4 at its vapour pressure of 7.8 bar to 9.1 bar at the prevailing ambient temperatures in the range 17°C to 22°C. The higher operating pressure was obtained by means of the compressor in the solvent recovery unit. The vessel S2 was provided for storage of the hydrocarbon mixture at atmospheric pressure when reflux was to be applied. For extraction without reflux the hydrocarbon mixture was stored in S3. Detailed operating procedures for the two cases are given in Section 6.4.2.

Ammonia was preferred as the dispersed phase since, in general, higher solvent to feed ratios would improve extract purity and higher surface areas for mass transfer would also result with the solvent phase dispersed.

In addition, since the hold-up of the dispersed phase was much less than that of the continuous phase it was an advantage to disperse ammonia. For the ternary system, Ammonia-Heptane-Cumene, it was subsequently found from equilibrium studies that the ammonia-rich phasewas the lighter phase and would therefore leave the top of the column for coalescence in the top settler. In practice, therefore, to avoid a large volume hold-up,the bottom settler was isolated from the equipment.

In normal operation, the R.D.C. and the top settler were initially charged with hydrocarbons and pressurised to the operating pressure; ammonia was pumped in subsequently. Non-return valves were provided in the inlet lines to prevent back flow. Ammonia, being the lighter phase, was fed to the bottom of the column. For reflux operation provision was made for introduction of the feed at the mid-section of the R.D.C; otherwise it entered at the top. The aromatic-rich top product, extract from the top settler was transferred into the evaporator of the solvent recovery unit for the removal of ammonia. The heavy raffinate from the R.D.C. passed into storage vessel S1. Aromatics-rich product collected at the bottom of the evaporator and flowed into the extract storage vessel S3.

6.1.1. The R.D.C.

The design, hydrodynamics and mass transfer efficiency characteristics of the R.D.C. were described in Section 4. The preferred limits for the ratios of compartment height,

disc diameter, stator opening and column diameter were given in Section 4.3. A list of recommended dimensions of the R.D.C. is also given in a nomogram prepared by Misek (32).

In general, in the design of an R.D.C. for a particular extraction duty, the column diameter and the rotor speed are the main variables to be determined. The diameter of the column is related to limiting hold-up, and flooding flowrates which are dependent upon the physical properties of the system.

Whilst this is the general procedure for estimating column diameter for a pilot scale R.D.C.,using liquid ammonia it was necessary to limit the volumetric capacity and hence the solvent inventory. A 5cm. internal diameter R.D.C. was considered sufficient to limit throughput without complicating construction or resulting in high 'wall effect during use. The height of the R.D.C. was 125cm. and it comprised two column sections each of 25 compartments. The shaft was a stainless steel rod 7.9mm. in diameter and was divided into two equal parts screwed together in the middle. It was supported by a p.t.f.e. bush inserted into a spider situated between the two column sections. This arrangement is shown in Figure 6.3. The bottom of the shaft rested in a p.t.f.e. bush centrally positioned in the bottom flange as shown in Figure 6.4.

Dimensions and other details of the column are summarised in Table 6.1. Stators and discs were made

Figure 6.4.

BOTTOM COLUMN SECTION

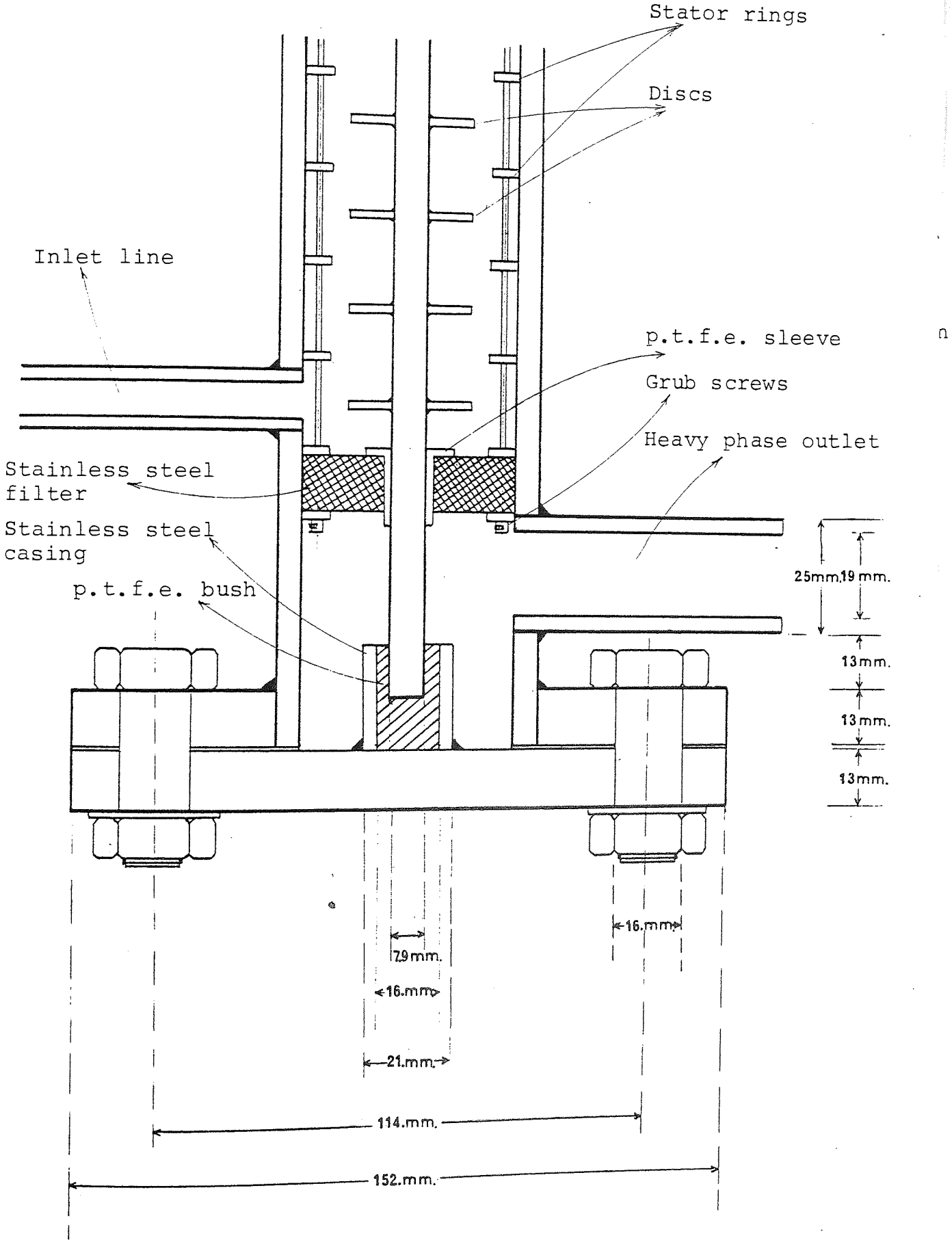
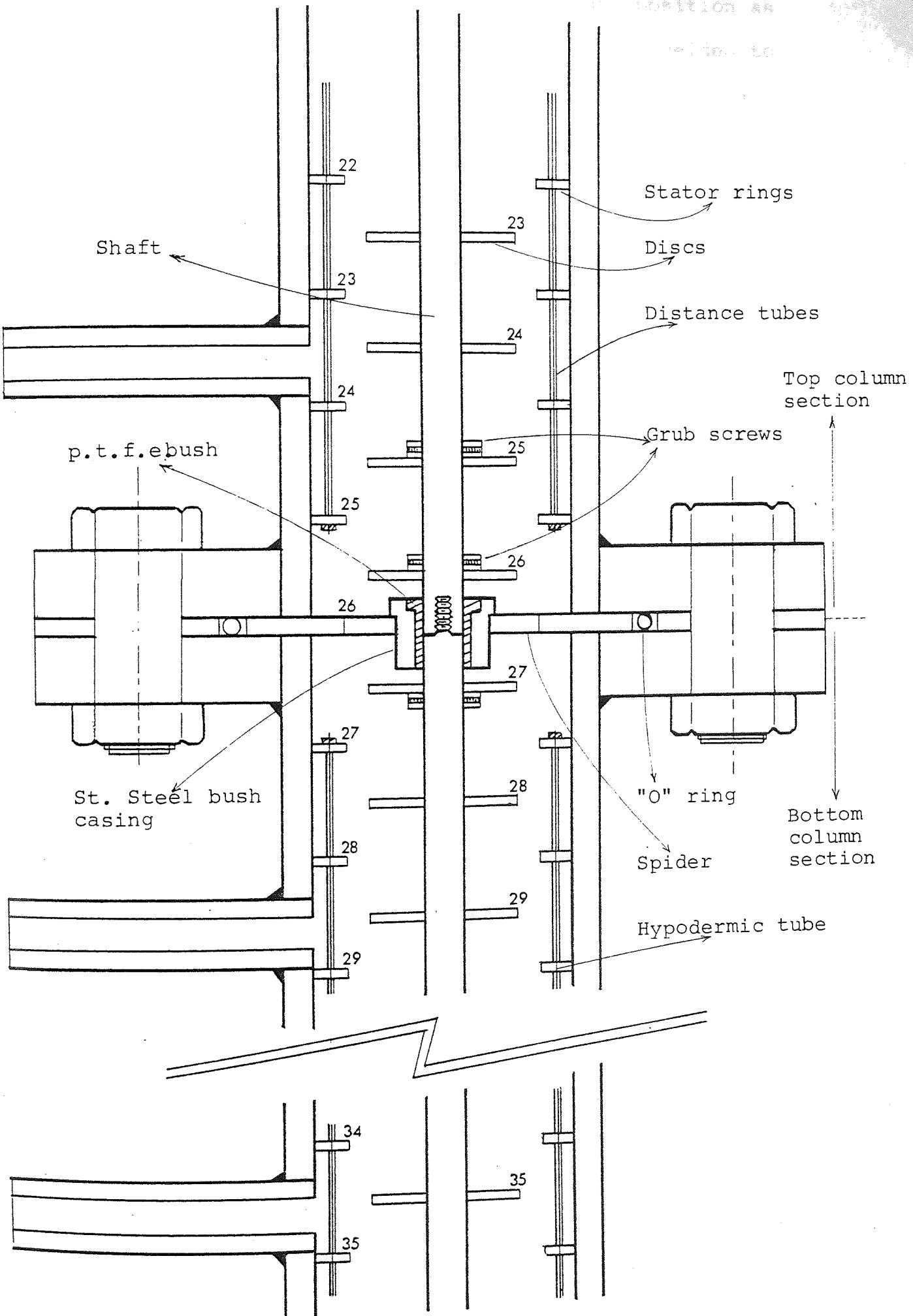


Figure 6.3.

THE RDC MIDDLE COLUMN SECTION



of 1.6mm. thick stainless steel sheet and position as shown in Figures 6.5. and 6.6. Discs were welded to the shaft and then machined to obtain a smooth, flat surface. Three discs near the middle of the shaft were fixed by grub screws so that they could be moved up or down for ease of assembly. The stator rings were supported by three equispaced distance tubes which were fastened to the top stator ring by grub screws. The rings were machined to a close fit with the column wall to avoid short-circuiting of liquids and the distance tubes were only 1.6mm. outside diameter to minimise disturbance of flow patterns. To isolate the phase inlets and outlets from the turbulence in the column and to assist phase separation, knitted mesh-type 13mm. thick stainless steel sections with 75% free volume were fixed to the top and bottom stator rings. To cope with the column operating pressure a Type 109B Crane single seal was assembled at the top of the rotor shaft.

The top of the column is illustrated in Figure 6.3. The seal was fixed to the shaft with grub screws and the shaft was machined to fit the inside diameter of the seal and the seal seat. A p.t.f.e. gasket was used to seal between the seal seat and top flange of the R.D.C. The seal and the seal seat were held together inside the top flange by socket head bolts. An aluminium bearing casing was bolted to this part of the construction. Here the shaft was supported by a radial bearing and a thrust bearing was used against axial thrust. A smaller diameter

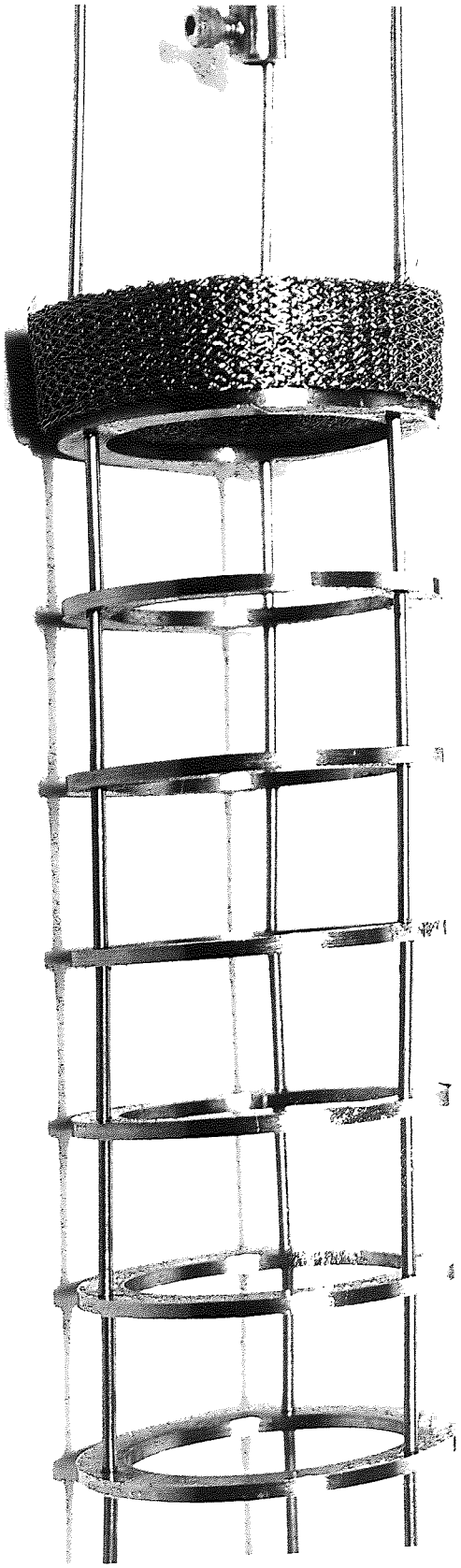


Figure 6.5.

ARRANGEMENT OF STATOR RINGS

Spacers comprise 1.6mm. outside diameter, 19.4mm. long stainless steel tubes. Bottom pad is a 75% free volume stainless steel knitmesh.

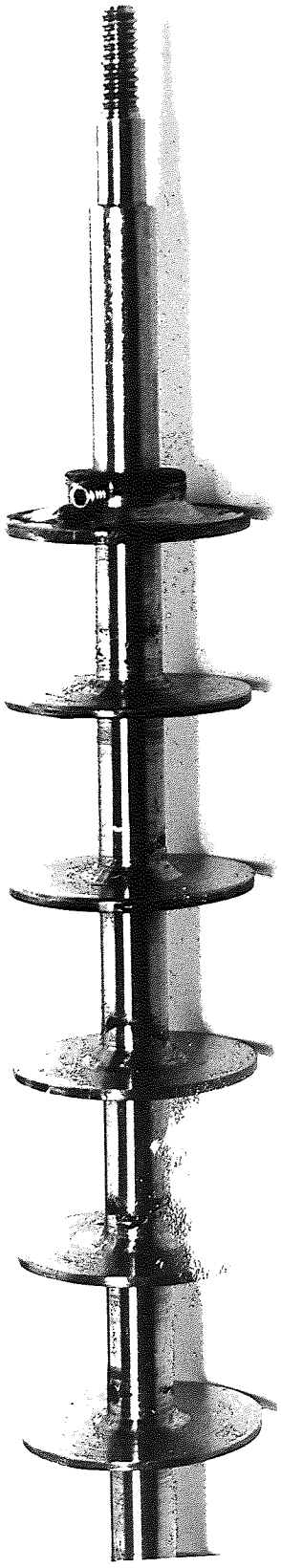


Figure 6.6.

DISCS FIXED TO UPPER SHAFT SECTION

Lower ones are welded. The top disc is fixed by grub screws.

Figure 6.7.

CONSTRUCTIONAL DETAILS OF TOP OF COLUMN

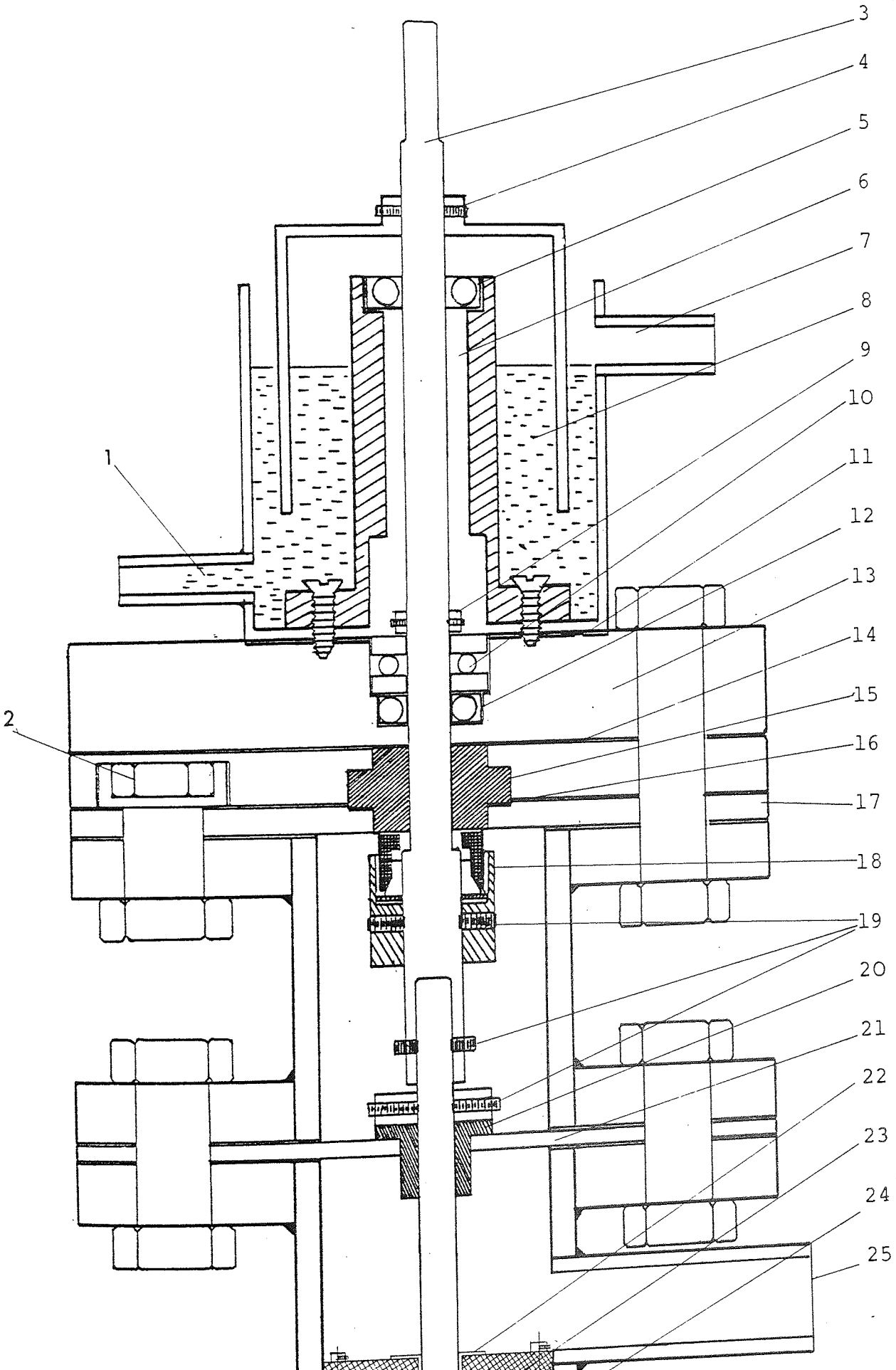


Figure 6.8.

CONSTRUCTIONAL DIMENSIONS OF TOP COLUMN SECTION

All dimensions are in mm.s

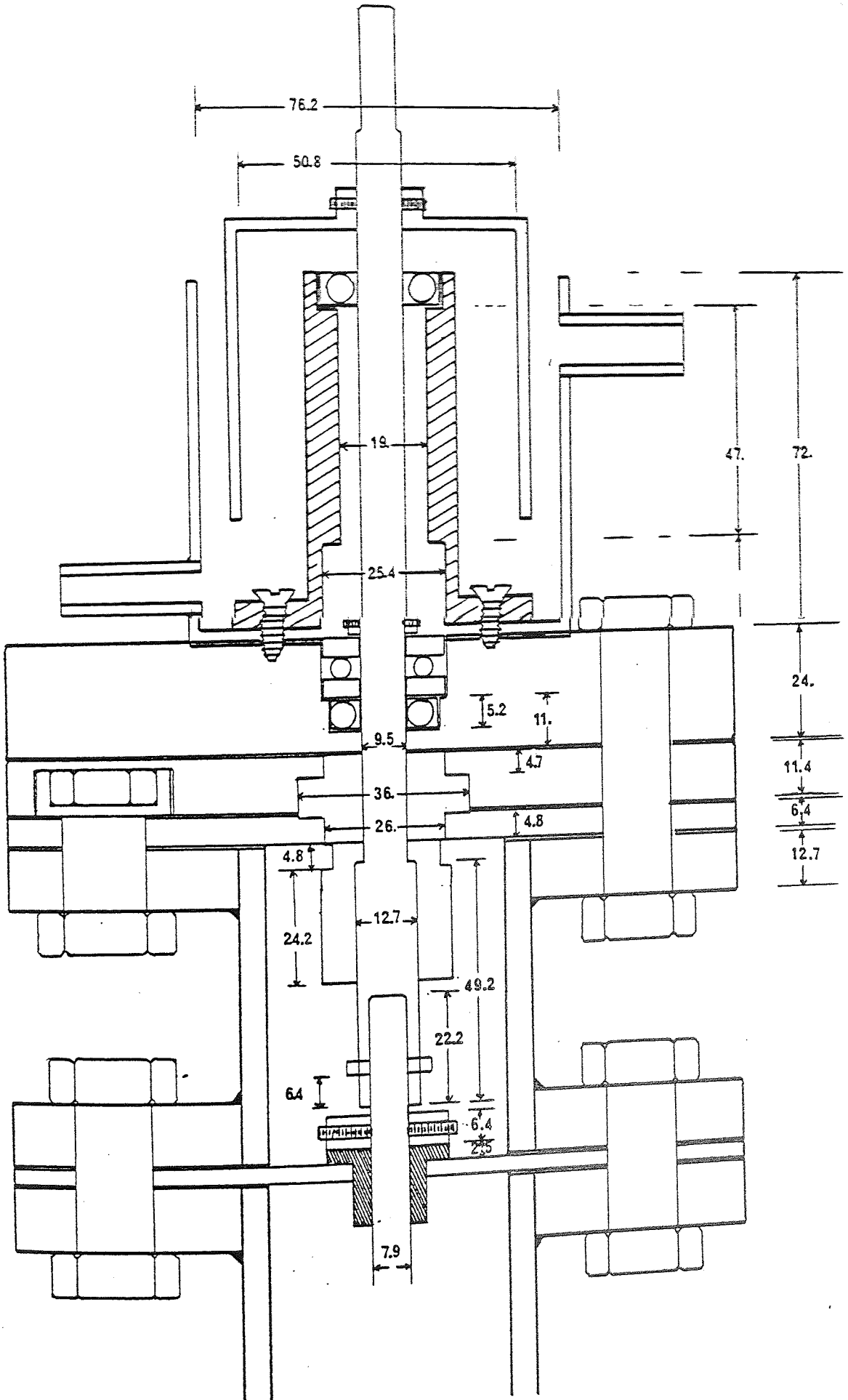


Table 6.1.

R.D.C. DIMENSIONS

Materials of Construction	Stainless Steel
Column inside diameter (D)	5.0 cm.
Column height	125.0 cm.
Column wall thickness	5.5 cm.
Stator and disc thickness	1.6 cm.
Rotor shaft diameter	0.79 cm.
Disc diameter (R)	2.9 cm.
Stator opening (S)	3.7 cm.
Compartment height (H)	2.1 cm.
Number of compartments	50
S/D	0.74
R/D	0.58
H/D	0.42
Operating pressure range	8.9 to 10.3 bar
Test pressure	20.4 bar
Maximum volumetric total capacity	60 lt/hr

collar was fixed to the shaft by grub screws and an oil reservoir was provided together with a water reservoir for the aluminium bearing casing. The oil reservoir contained Type Tellus F3 Shell oil for lubrication of the bearings. The shaft was also supported by a thrust bearing mounted on top of the oil reservoir. A water reservoir was provided above the seal; this was flushed through with water during operation to absorb any seepage of ammonia. Full details of the construction of the top column section are given in Figure 6.8. The rotor shaft was driven via a horizontal pulley arrangement as shown in Figure 6.9.

6.1.2. Settlers

Following extraction the dispersion produced in the mixing compartments must be separated by coalescence of the dispersed phase. This can be achieved either at the top, or bottom of the column, or in an external gravity settler.

Two external settlers were provided and were connected to the R.D.C. by means of compression couplings. Each comprised a cylindrical vessel with 53 cm. wedge length and 26.6 cm. internal diameter providing a hold-up of 29.5 litres. This allowed a minimum of 0.5 hr. of settling time based on a maximum total volumetric capacity of the R.D.C. of 60 l/hr.

Subsequently, equilibrium studies indicated that

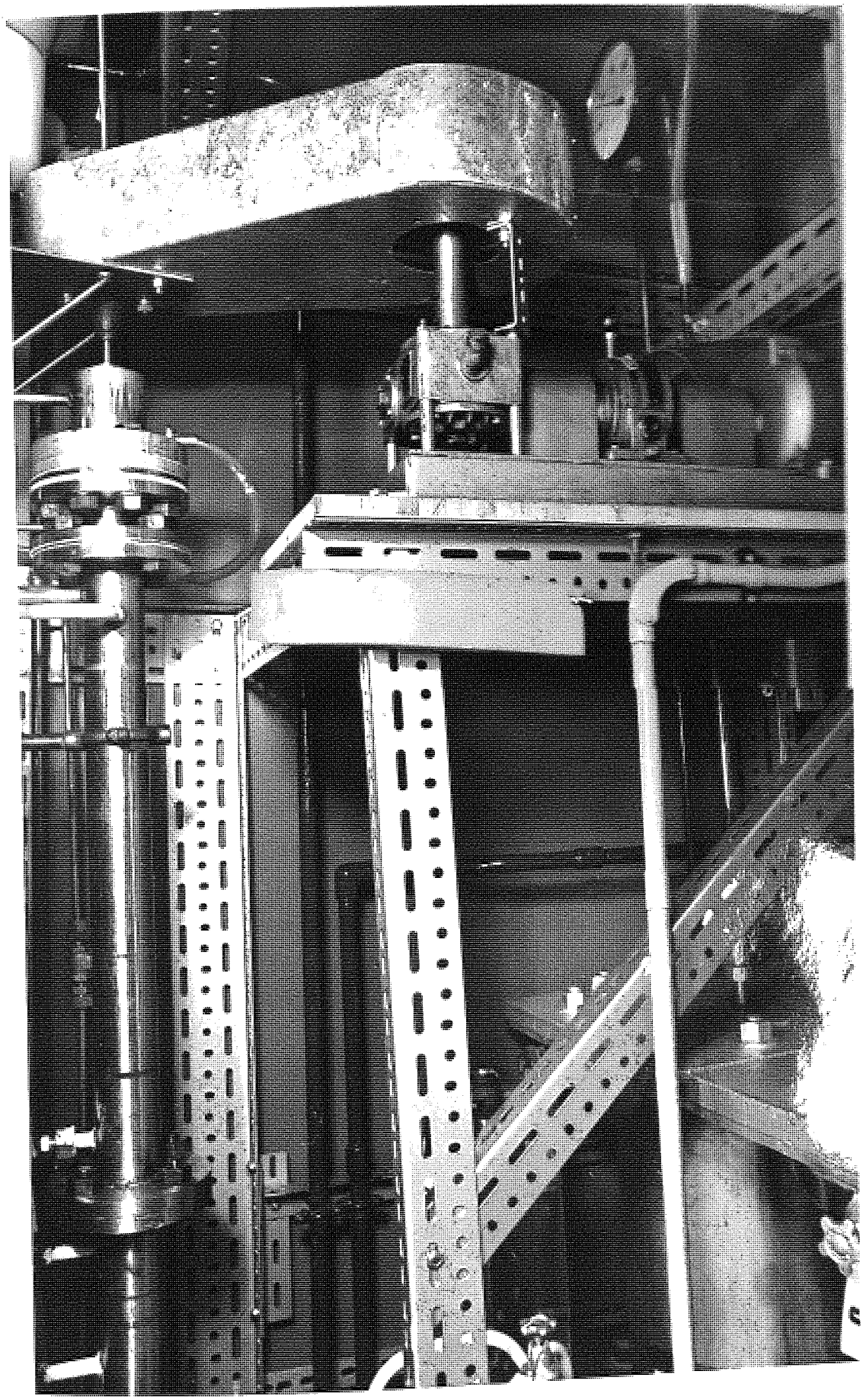


Figure 6.9.

DRIVE FOR R.D.C. SHAFT

flameproof motor.

the ammonia rich phase would constitute the light phase. Hence, ammonia, as the dispersed phase, was introduced into the bottom of the R.D.C. so that settling would occur in the top settler. For this reason the bottom settler was isolated from the system to prevent large unnecessary hold-ups.

Settler details are shown schematically in Figures 6.10(a) and 6.10(b). Each vessel was of 10 inch nominal bore i.e. 27.3 cm. outside diameter with 3.4 mm. wall thickness. The flanges were bolted to the square end plates as shown in Figure 6.11., a seal being provided by an 'O' ring of nitrile rubber which is resistant to both ammonia and hydrocarbons.

Each vessel was equipped with a sight glass for observation of the interface level; this was built into the flat end as shown in Figure 6.11. Transparent Polycarbonate CR 39 sheet was used to withstand the operating pressure but, since this is not resistant to ammonia and hydrocarbons, 0.5 mm. thick f.e.p., i.e. fluorinated ethylene propylene, sheet was provided as a lining. A p.t.f.e. sheet of 0.8 mm. thickness was used as gasket material.

Each settler was provided with two outlets, each of 7.6mm. inside diameter, and located at the opposite end to the inlet. The light phase from the top settler was transferred to the solvent recovery unit; the heavy phase

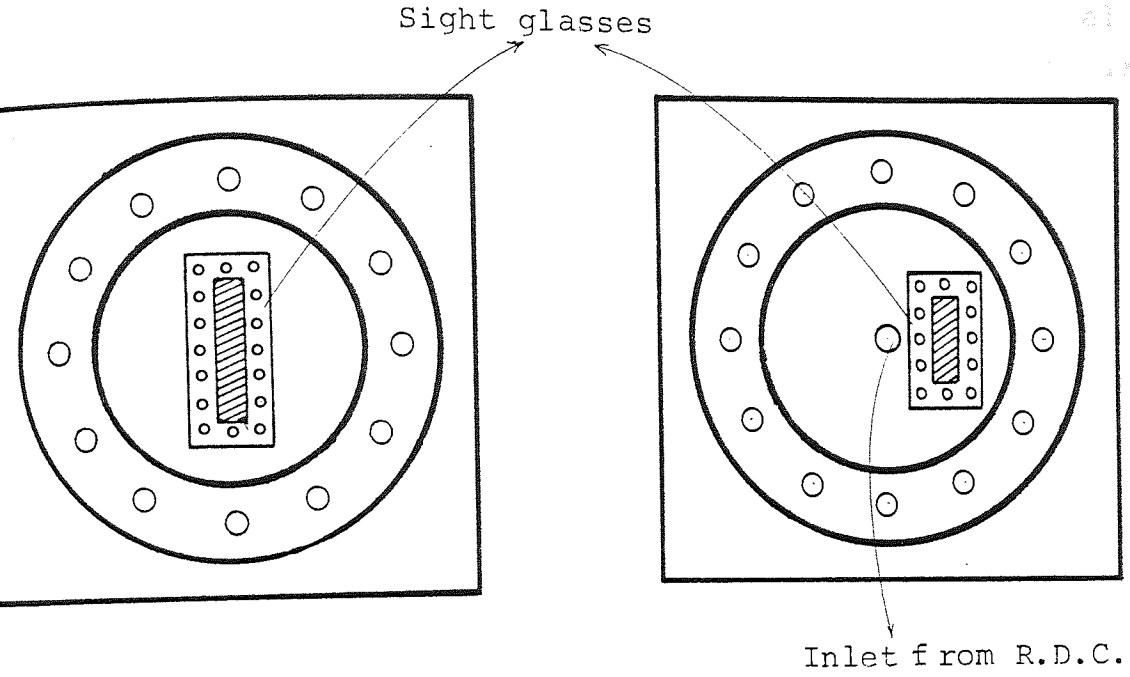


Figure 10(a)

NGES (1), (2), and (3) ON THE LEFT, FLANGE (4) ON THE

RIGHT

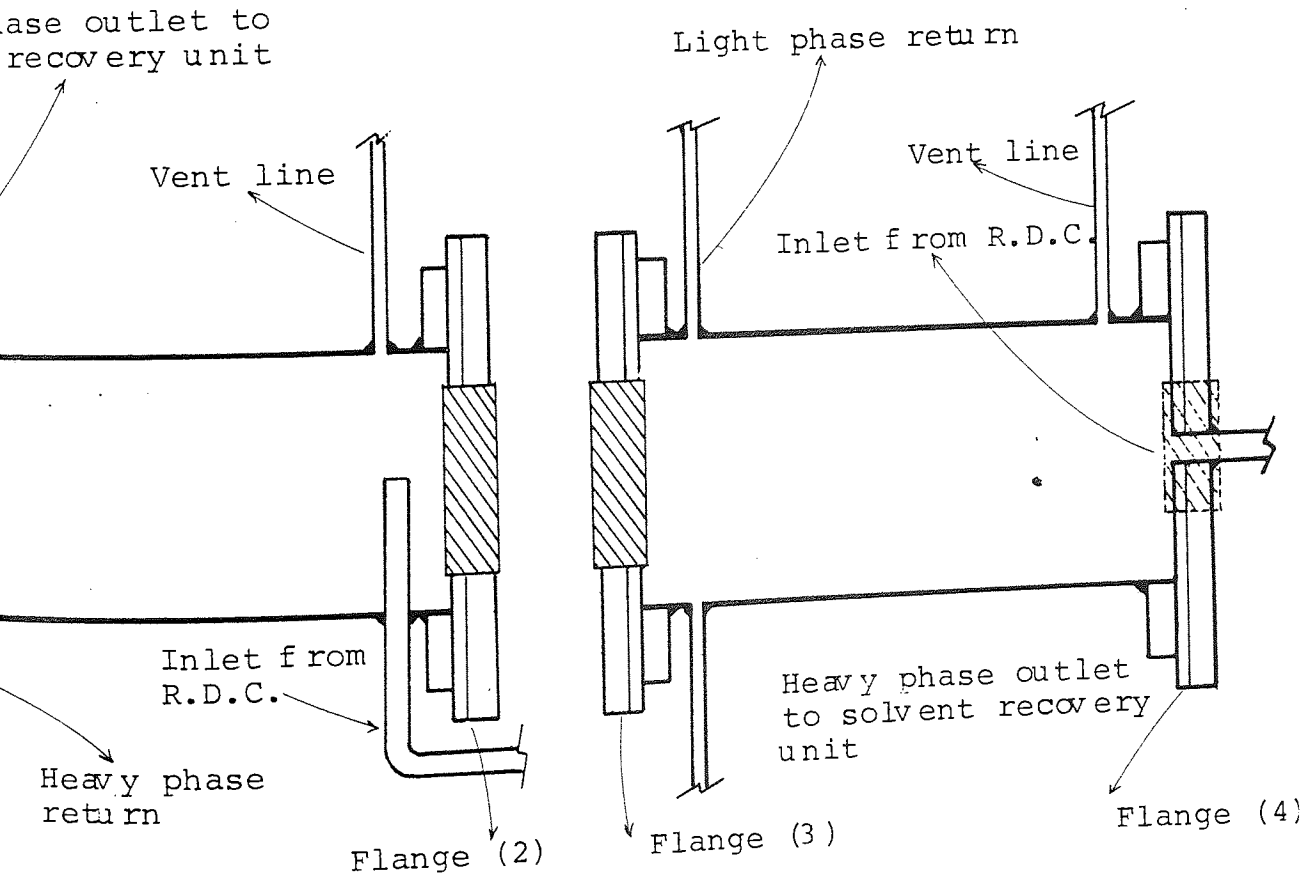


Figure 6.10(b)

TOP SETTLER ON THE LEFT BOTTOM SETTLER ON

THE RIGHT

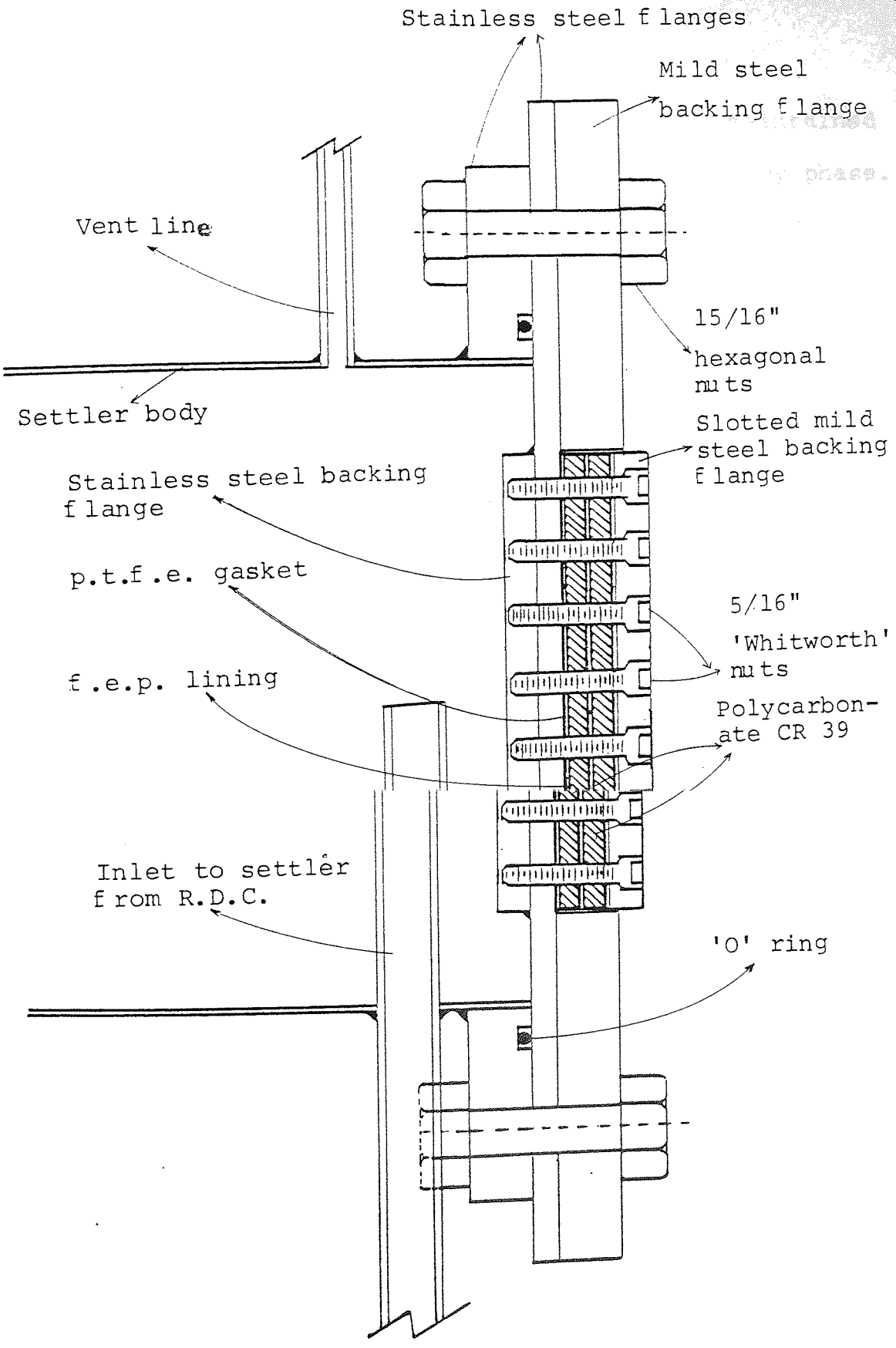


Figure 6.11.

ARRANGEMENT OF SIGHT GLASSES ON TOP AND BOTTOM SETTLERS

was returned to the R.D.C. The interface was maintained by controlling the flow rate of the returning heavy phase. Alternatively, for operation with a different ternary system, provision was made for use of the bottom settler with the heavy phase transferring to the solvent recovery unit and the light phase returning to the R.D.C.

Each settler was provided with a vent line including a stainless steel pressure gauge (0-300 p.s.i.). A pressure switch was fitted to the vent line of the top settler; details of this pressure switch are given in Section 6.1.4.

6.1.3. Storage Vessels

Five cylindrical storage vessels S1 to S5 were provided for storage of feed, solvent, modifying agent and the top and bottom products. S1, S2 and S3, for hydrocarbons storage, had a combined capacity for 60 litres of hydrocarbons. S4 was for ammonia storage at its saturated vapour pressure, i.e. 7.8 bar to 9.1 bar at ambient temperatures of 17^{o}C to 22^{o}C. Vessel S5 was for storage of solvent-modifying agent, e.g. mono-methylamine, or water

Each vessel was of similar construction. The stainless steel body was bolted to square stainless steel flat, end flanges of 9.5mm. thickness, backed by mild steel flanges of 25.4mm. thickness. The seal between the flanges was provided by nitrile 'O' rings. Each vessel was tested hydraulicallyat 20.7 bar and gas tested

with nitrogen, at 13.8 bar.

Dimensions and details of the vessels are given in Table 6.2. Vessels S1, S3, S4 and S5 were provided with level gauges. These had globe valves for emergency shut-off in the event of the gauge glass breaking and were protected by a tubular type brass shield. The assembly of the gauges is shown in Figure 6.12.

The duties of vessels S1, S2, and S3 depended upon whether the R.D.C. was operated with or without reflux. For reflux operation the design allowed for feed to enter the R.D.C. in the middle; for operation without reflux the feed entered at the top of the R.D.C.

Piping

The piping arrangement within the extraction plant is summarised in Table 6.3.

Generally, all lines were of ¼" n.b. stainless steel, 7.6 mm. inside diameter with 3 mm. wall thickness. Pipe joints were by, welding and 'Ermeto' compression couplings. Pressure relief lines were of 25.4 mm. inside diameter seamless iron pipe.

Figure 6.12

END DESIGN OF TANK SHOWING

SIGHT GLASS CONNECTION

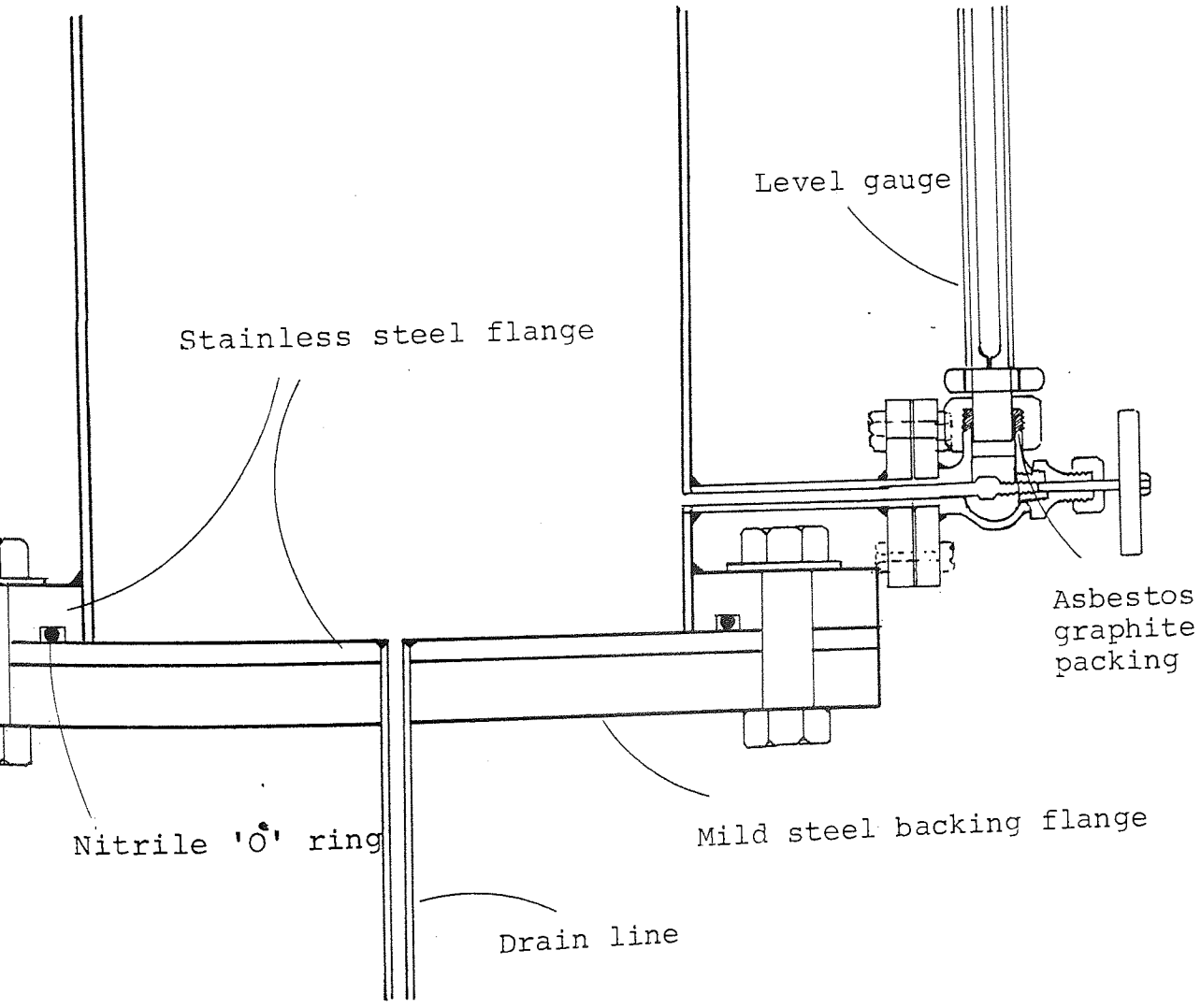


Table 6.2.

DIMENSIONS AND DUTIES OF STORAGE VESSELS

Diameter cm.		Height cm.	Capacity litres	Duty with/without reflux use
Inside	Outside			
31.6	32.4	45.7	37.7	Storage of raffinate (N.O. and R.O.)
31.6	32.4	45.7	37.7	Storage of feed (R.O. only)
31.6	32.4	45.7	37.7	Storage of extract (R.O. only) Storage of feed (N.O. only)
31.6	32.4	60.9	50.3	Storage of ammonia (N.O. and R.O.)
26.6	27.3	45.7	25.5	Storage of modifying agent (N.O. and R.O.)

Note: In this table and subsequent descriptions, N.O. = Normal Operation, R.O. = Operation with Reflux.

The piping arrangement shown in Figure 6.2. also allowed liquids to be transferred between vessels S1 and S2 and S3 for cleaning or maintenance requirements.

Table 6.3.

ARRANGEMENTS AND INTERCONNECTION OF EQUIPMENT

Refer to Figure 6.2.

Vessel S1

a) Vent via valve V1, and line welded centrally into top (N.O. and R.O.). (Pressure gauge PI5 was branched from this line).

b) Drain via valve V5 and line welded centrally into bottom (N.O. and R.O.).

c) Inlet line welded into side 12cm. from bottom. Branched to 2 lines, one for transfer of bottom product (raffinate) if interface in top settler via V42; other for transfer of raffinate via V52 if interface in bottom settler (N.O. and R.O.).

d) Outlet line; branched from drain line for transfer of hydrocarbons, on completion of a run into S2 via V4 and V11 (R.O.); or into S3 via V4, V7 with pump P2 operating (N.O.).

Vessel S2

a) Vent via valve V8 and line welded centrally into top. (N.O. and R.O.). (Pressure gauge PI4 branched from this line).

b) Drain via valve V10 and line welded centrally into bottom. (N.O. and R.O.).

c) Inlet line welded into side about 30cm. from bottom. Branched to 2 lines, one for initial charging of the system with feed stock via valve V9; other for transfer of hydrocarbons into the vessel via valves V6 and V7 and with pump P2 operating. (N.O. and R.O.).

d) Outlet line branched from drain line for transfer of hydrocarbons via valve V11 with pump P2 operating i) into S3 via V7 and V16 (N.O.), ii) back to S2 via V7 and V6 for mixing aromatic and non-aromatic constituents of feed stock (N.O. and R.O.), iii) into the R.D.C. via CV2, rotameter R2, NRV5, V13, V14, V15 (R.O.).

Vessel S3

a) Vent via valve V20 and line welded centrally into top. (N.O. and R.O.). (Pressure gauge PI3 branched from this line).

b) Drain via valve V17 and line welded centrally into bottom. (N.O. and R.O.).

c) Inlet line welded into side about 30cm. from bottom. Branched to 2 lines, one for the inlet of hydrocarbons from vessel S1 or S2 via valves V7 and V16 with P2 operating (N.O.); other inlet of hydrocarbons from evaporator via NRV3, V54 (R.O.).

d) Outlet line branched from drain line and served for i) delivery of hydrocarbons to top of R.D.C. as feed via V18, CV3, rotameter R3, V24 and NRV4 (N.O.), ii) delivery of hydrocarbons to top of R.D.C. via same line and as reflux (R.O.).

Vessel S4

... V24 and the line welded centrally

into top (N.O. and R.O.). (Pressure gauge PI1 branched from this line, a pressure relief line branched, for release of excessive pressure via V75, PSV2 into water tank, a balance line for pressure therefore liquid level in S4 also branched connecting S4 to condenser).

b) Drain via valves V25, V26 and V23. (The line was used only to drain water after washing and before charging with ammonia). Line welded centrally into bottom.

c) Inlet line welded into side about 30cm. from bottom, to allow ammonia flow into vessel from the condenser via V69, NRV2 and V41 (N.O. and R.O.).

d) Inlet line for modifying agent for solvent from S5 via V40. Line welded into side about 30cm. from the bottom (N.O. and R.O.).

e) Pressure balance line, connecting S4 to S5 via V35, during charging S4 with modifying agent, line welded into top about 3cm. off centre.

f) Inlet line for modifying agent via V31 with pump P1 operating and modifying agent supplied from S5 via V39, V27. (This line was for use if S4 pressure exceeded that in S5 i.e. S4 containing ammonia). Line welded into side about 30cm. from bottom.

g) Inlet line via V30, NRV1, V28, V27, V31 with P1 operating, for charging S4 with ammonia from cylinder connected other side of V30. Line also

used for pressure testing piping and vessels between runs as necessary.

h) Outlet line from i) via V25, CV1, rotameter R1, V45 and NRV6 with pump P1 operating, into the bottom of the R.D.C. ammonia supply as solvent (N.O. and R.O.) ii) branching from the same outlet line allowing ammonia to flow into evaporator via V25, V26, V58, V55 and PR1 - hence by-passing extractor and completing a refrigeration cycle. (Line used before each run until solvent recovery operation reached a steady state e.g. for about 20 to 30 minutes).

Vessel S5

a) Vent via valve V36 and line welded centrally into top (N.O. and R.O.). (Pressure gauge PI2 branched from this line).

b) Drain via valves V27, V26 and V23 and line welded centrally into bottom. (Drain line only for draining water after washing).

c) Pressure balance line, connecting S5 to S4 via V35 (see Vessel S4 line (e)). Line branching from vent line.

d) Outlet line for the modifying agent; same as drain line via V39, V27, V31 with P1 operating (see Vessel S4, line (f)).

e) Outlet line for modifying agent flow into S4 via V40 when S4 does not contain ammonia.

6.1.4. Auxiliary Equipment

Pumps

Three pumps were provided for pumping solvent, feed or reflux respectively. Each pump was of similar design namely a 'Pygme' piston-type pump supplied by Grosvenor Pumps Ltd. and driven by a 0.186 k.W., 3 phase T.E.F.C. motor. Each pump was capable of pumping 0.035 litres per second against 13.8 bar pressure. The pump head was of stainless steel with a 'Chevron' type gland of nitrile rubber, recommended for handling ammonia and hydrocarbons at ambient temperature. The gland rings could be changed without removal of the pump head. Each pump incorporated a spring loaded non-return valve and a by-pass line between the suction and delivery sides containing a diaphragm valve to assist with control of flowrate and pressure. The pump was not self-priming; therefore, application of vacuum was required for removal of air, or non-condensibles, from the pump prior to pumping.

Rotameters

Rotameters were installed in the solvent, feed and reflux lines for flowrate measurement. (Their full specifications are given in Appendix (3)).

The tubes were tempered borosilicate glass of 6.4 mm. bore with a maximum operating pressure of 35 bar

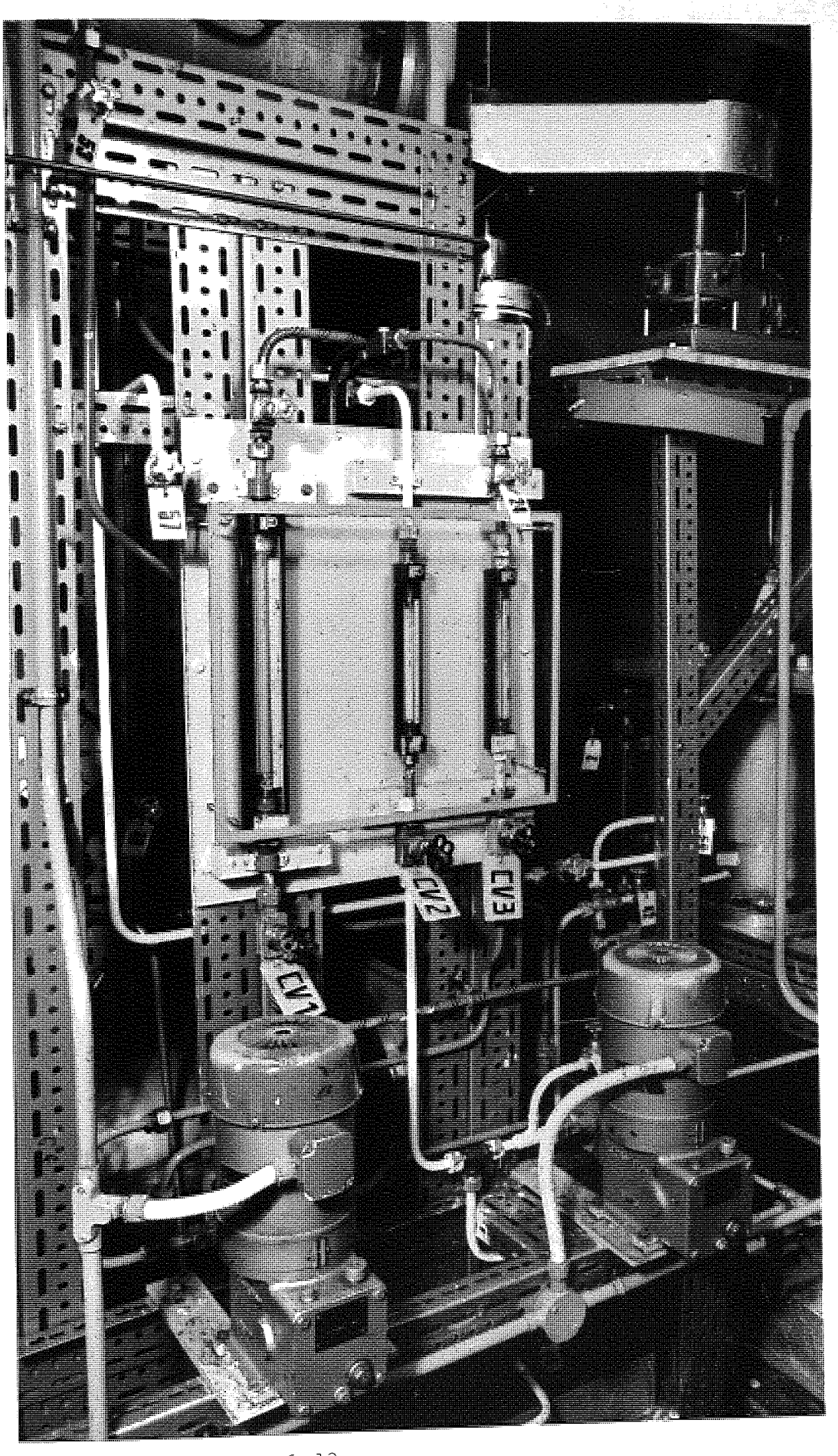


Figure 6.13.

SOLVENT TRANSFER PUMPS AND ROTAMETERS

P3 the feed transfer/reflux pump (left); P2 the feed pump for

and of 12.8 mm. bore with a maximum operating pressure of 21 bar. The end seals were provided by nitrile 'O' rings. The floats of R1 and R2 (Figure 6.2) were of stainless steel; the float of R3 was tantalum. The tubes were fitted with shields of toughened glass.

Valves

The range of valves used are summarised in Table 6.4.

Initially most of the stop valves were welded into position; some porous welds were, however, detected by testing, due to the small bore and inaccessibility of some lines. Later, the use of male stud compression couplings proved more efficient with Loctite Pipe Sealant No. 572 as jointing compound on the threads. These valves were recommended for use with hydrocarbons and ammonia mixtures, but during commissioning the p.t.f.e. diaphragms tended to rupture; use of vacuum accelerated the failure rate. Application of vacuum was subsequently eliminated from the operating procedure (Section 6.4.). Control valve CV1, fitted in the ammonia line, required periodic repacking of the spindle stuffing box with asbestos graphite to rectify leaks.

Non-return valves were fitted in any line where flow could be reversed due either to the high solubility of ammonia in aromatic hydrocarbons, or an excess of upstream pressure over the downstream pressure. (These

Table 6.4.

THE VALVES USED, TYPE AND DUTY

Valve Type	Duty
Stop Valves a) Diaphragm Type	¼" N.B. lines provided with Saunders stainless steel/mild steel body, p.t.f.e. diaphragm type screwed ends. For isolation or to stop transfer of liquid purposes.
b) 'Chevron' Type	Fitted in ½" N.B. and 3/4" N.B. lines for isolation purposes. (Valves V55, V60, V61, V62, V66, V67, V69, V85). Stainless steel body, flange fitting.
Control Valves	Provided in ¼" N.B. lines for fine control of flow. Hindle stainless steel needle valves with screwed ends, metal to metal seats, stuffing-box spindle packed with asbestos-graphite (CV1, CV2, CV3).
Non-return Valves	Fitted horizontally in selected ¼" N.B. lines to eliminate reverse-flow. Hindle stainless steel ball and seat type valves, screwed ends.
Pressure Relief Valves	
a) PSV1	Inserted in vent line of S4. Spring-loaded type, set to relieve at 17.2 bar. Supplied by Henry Pressure Relief Valves (special for ammonia service.)
b) PSV2 & PSV3	Stainless steel spring-loaded Hindle valves

Valve Type	Duty
b) PSV2 & PSV3 cont.	set to relieve at 13.8 bar. Located in ½" N.B. lines branching from vent lines of S6 and S7.

valves needed occasional cleaning of steel balls and seats in service).

A 50 gallon water tank was provided to receive the discharges from the safety valves; to prevent back flow of water a small tee venting to atmosphere was fitted in the line to act as a syphon break. PSV2 and PSV3 were tested with nitrogen and set to relieve at the maximum operating pressure at 13.8 bar. (Periodic cleaning of valve seats and replacement of springs were necessary in service as the valves tended to leak after use).

Pressure Switch

A Danfoss pressure switch was installed on the top settler to cutout the pumps, the compressor and the R.D.C. drive motor if the system pressure exceeded the design operating pressure. This was a Type RT 5A No. 175047/456 switch set to cut out at 12.4 bar. The interconnection of the pressure switch, control and other protection switches in the electric circuit is shown in Appendix 4.

The R.D.C. Drive Motor

The R.D.C. agitator shaft was driven by a $^{1}/_{3}$ h.p. flame proof, FLP 2546, Group No. II AC motor. This was a Type BCF 2410 motor equipped with a gear box providing infinitely variable speed. Torque from the motor was transmitted via horizontal pulleys of 20 cm. diameter (drive shaft) and 5 cm. diameter (R.D.C. shaft). The pulleys and drive belt were covered by a galvanized iron

guard. This arrangement is shown in Figure 6.9 .

The speed of the shaft was measured by a Comark electronic tachometer. The maximum obtainable speed was 900 r.p.m.

Fume Cabinet and Fan

The complete extraction plant was built into a fume cabinet with a sliding access door. The atmosphere from the cabinet was vented from the building at high level. The fan motor extracted 0.34 m^3 of air per second and was normally operated 24 hours a day.

Water Spray

An emergency water spray system was installed for use in case of a burst pipe joint, or other malfunction, causing a major leak of ammonia. This water spray system comprised a 25 mm. diameter copper pipe line containing numerous 3.1 mm. diameter holes. It extended inside the fume cabinet, over the storage vessels and R.D.C., and outside, above the evaporator. It was activated by an alarm button connected to a solenoid in the town water mains; this also operated a warning bell.

6.2. The Solvent Recovery Unit

Ammonia was recovered from the extract phase using a solvent recovery unit consisting of an evaporator, compressor and condenser. A flow sheet of the unit is shown in Figure 6.14. The ammonia rich phase, ie. the

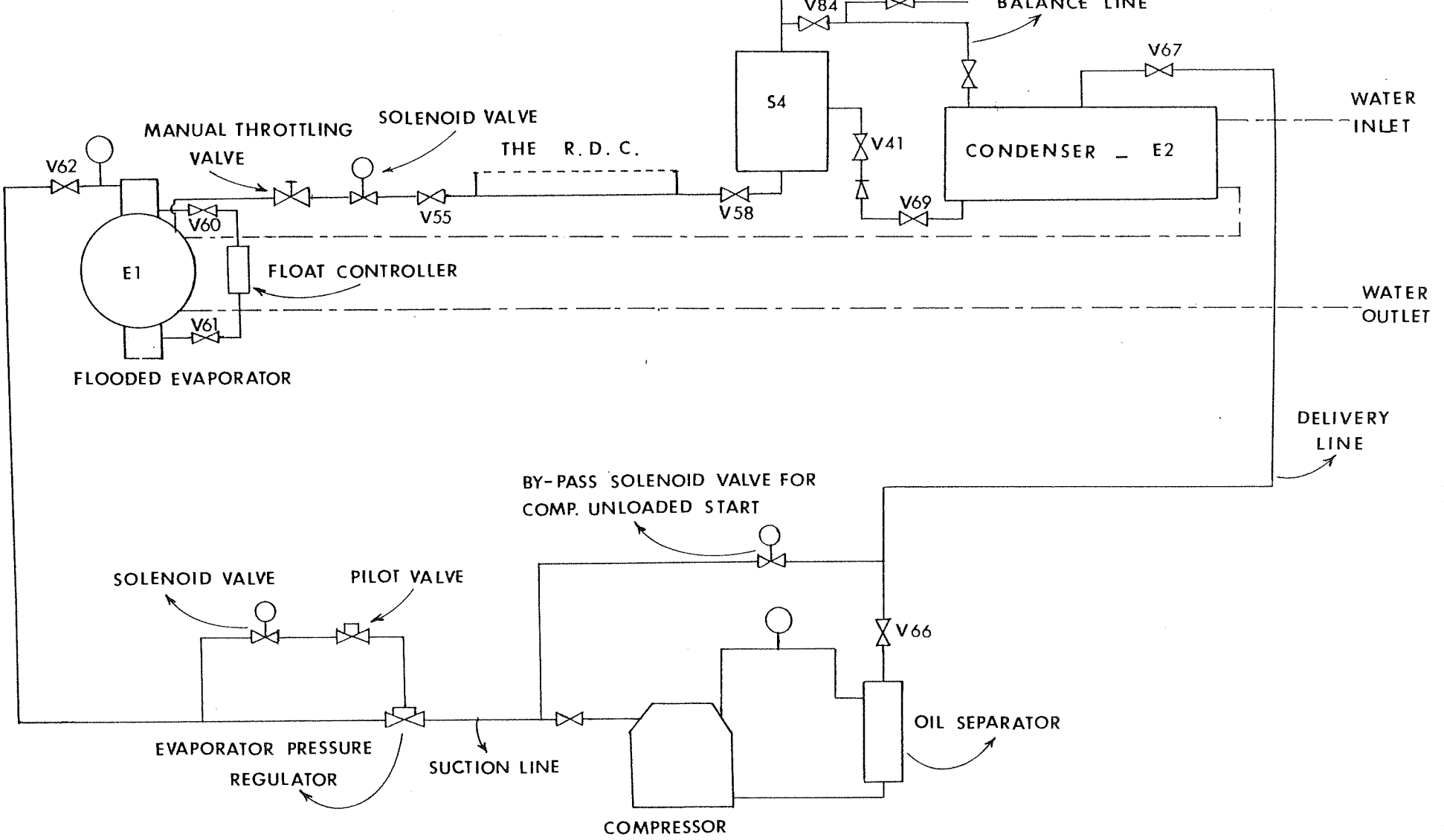


Figure 6.14.

SOLVENT RECOVERY CYCLE

extract, left the contactor via the top settler and passed through a pressure reducer valve. The evaporating pressure could be altered by adjusting this throttle valve. Ammonia was then flashed into the evaporator and the super-heated gas passed to the compressor. Hydrocarbons were collected at the bottom of the evaporator. Compressed ammonia was finally subcooled in the condenser and flowed to the liquid receiver, i.e. storage vessel S4. Liquid ammonia was pumped from vessel S4 into the R.D.C. and settler to complete the cycle.

A by-pass line was provided, connecting the liquid receiver to the evaporator. This enabled ammonia to be circulated around the solvent recovery unit to allow steady state operating conditions to be reached before it was introduced into the R.D.C. A balance line was provided between the liquid receiver, S4, and the condenser; ammonia flowrate into S4 could be altered by adjusting valve V85 in this line. The full construction and operating details are given in Sections 6.2.1. to 6.2.3. and 6.3.2.

6.2.1. The Evaporator

The evaporator shown in Figure 6.15 was a Goedhart flooded ammonia liquid chiller and separator type MC44 16/9. It comprised a shell and tube exchanger to evaporate a maximum of 90 l/hr. liquid ammonia. Design calculations and construction details are included in Appendix 5A.

The evaporator was provided with a liquid level control,

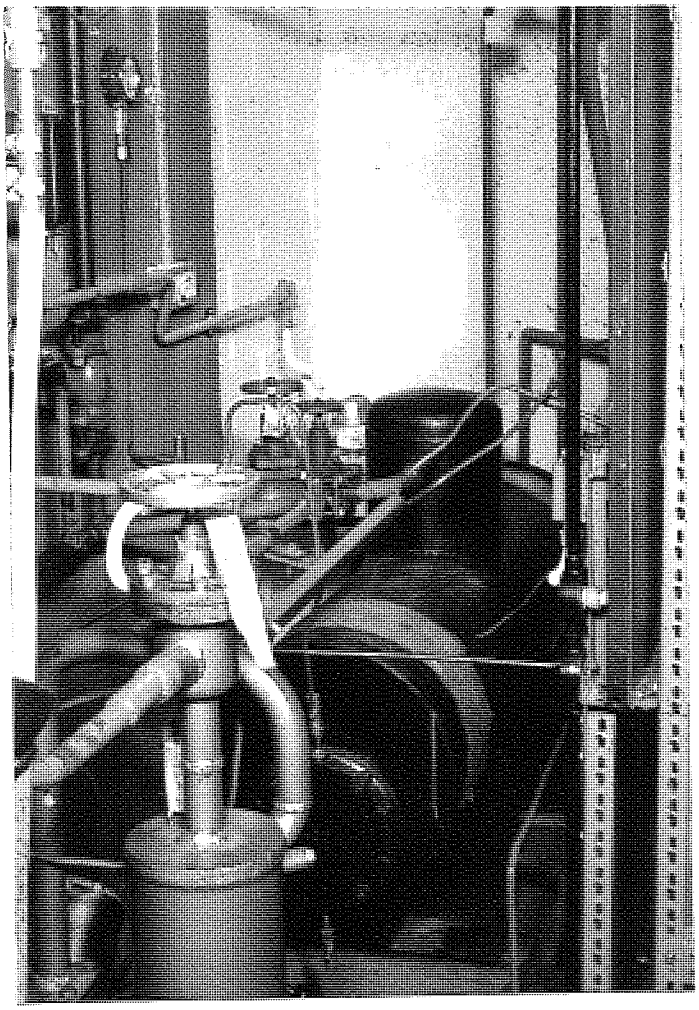


Figure 6.15.

THE EVAPORATOR

Specification:

Duty	19.34 kJ/s.
Evaporating temperature	-9.4°C
Maximum water temperature	21°C
Cooling surface area	3.68 m^2
Number of tubes	44
Cooling length	1400 mm
Number of passes	14
Water pressure drop	4 mm. wg.

as shown in Figure 6.16. The level control consisted of a float housing and an amplifier. The float housing was fitted at the average liquid level required, about mid-level. It was of cast iron with a ball float provided with an armature surrounded by a pilot coil; movement of the float caused the armature to move in or out of the pilot coil. The amplifier was provided with a mains transformer for connection to the 380 V, 50 Hz, 3 phase electrical supply.

The inlet line to the evaporator was equipped with a Danfoss Type EVJDA 3, solenoid valve followed by a Danfoss Type 6F manual throttle valve. The solenoid valve was normally closed; when the compressor started it was energised and opened. The throttle valve served to adjust the flow into the evaporator and hence maintain the evaporating pressure at the required valves (1 to 3 bar). Evaporated ammonia flowed from the top of the separator and liquid tank; this line contained a pressure gauge to indicate the evaporating pressure. Pressure regulating valves were installed in the suction line to maintain the evaporating pressure constant; these valves are shown in Figure 6.16. The valves consisted of a main valve, a pilot valve and two solenoid valves, one between the main valve and the pilot valve and the other in the compressor by-pass line. The main valve was a Type PHS20 and a minimum of 0.07 bar pressure-drop across the valve was required to open it. The pilot valve Type CVM was manually regulated to provide flexibility with regard to

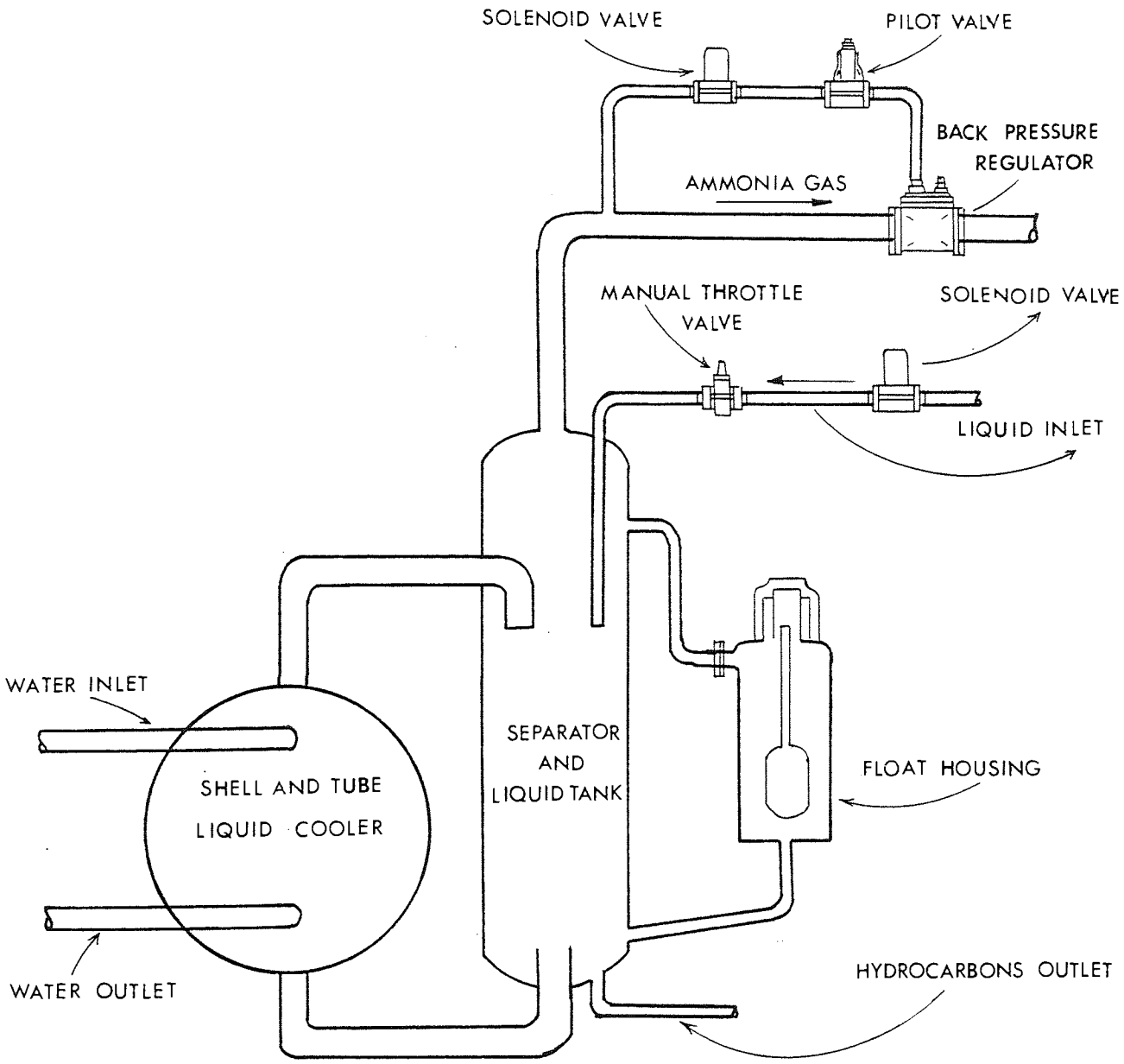


Figure 6.16.

THE EVAPORATOR/SEPARATOR

the suction and delivery pressures in the solvent recovery unit.

6.2.2. The Compressor

The compressor was a J. & E. Hall $2^{1}/8$"x 2", 4 cylinder compressor direct driven by a 10 h.p. electric motor. The cylinders were positioned radially in banks of two around the upper half of the crankcase. The compressor was able to operate to unload one bank of two cylinders; this provided 50% unloaded start with 50% capacity reduction.

The suction inlet was at the gland end of the crankcase. Ammonia vapour entered the crankcase through a combined suction strainer/stop valve bolted directly to the compressor inlet flange. Both the delivery and suction valves were mounted on the valve plate; the delivery valve was on the upper side within the cylinder cover, and the suction valve on the underside in the cylinders. The cylinder head was water cooled, for which a flow of 0.73 litres/min. at an inlet temperature of $32^{o}C$ was recommended. The detailed specification of the compressor, shown in Figure 6.17, is given in Appendix 5B.

6.2.3. The Condenser

A water cooled shell and tube type exchanger shown in Figure 6.18 was used to condense the gaseous ammonia leaving the compressor. The water was on the tube side.

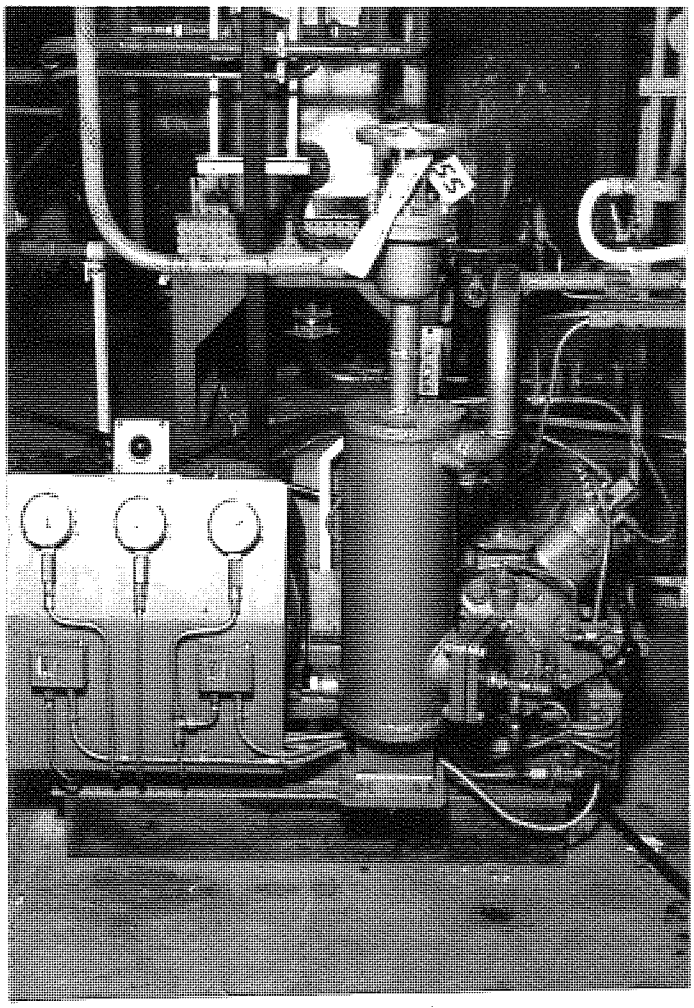


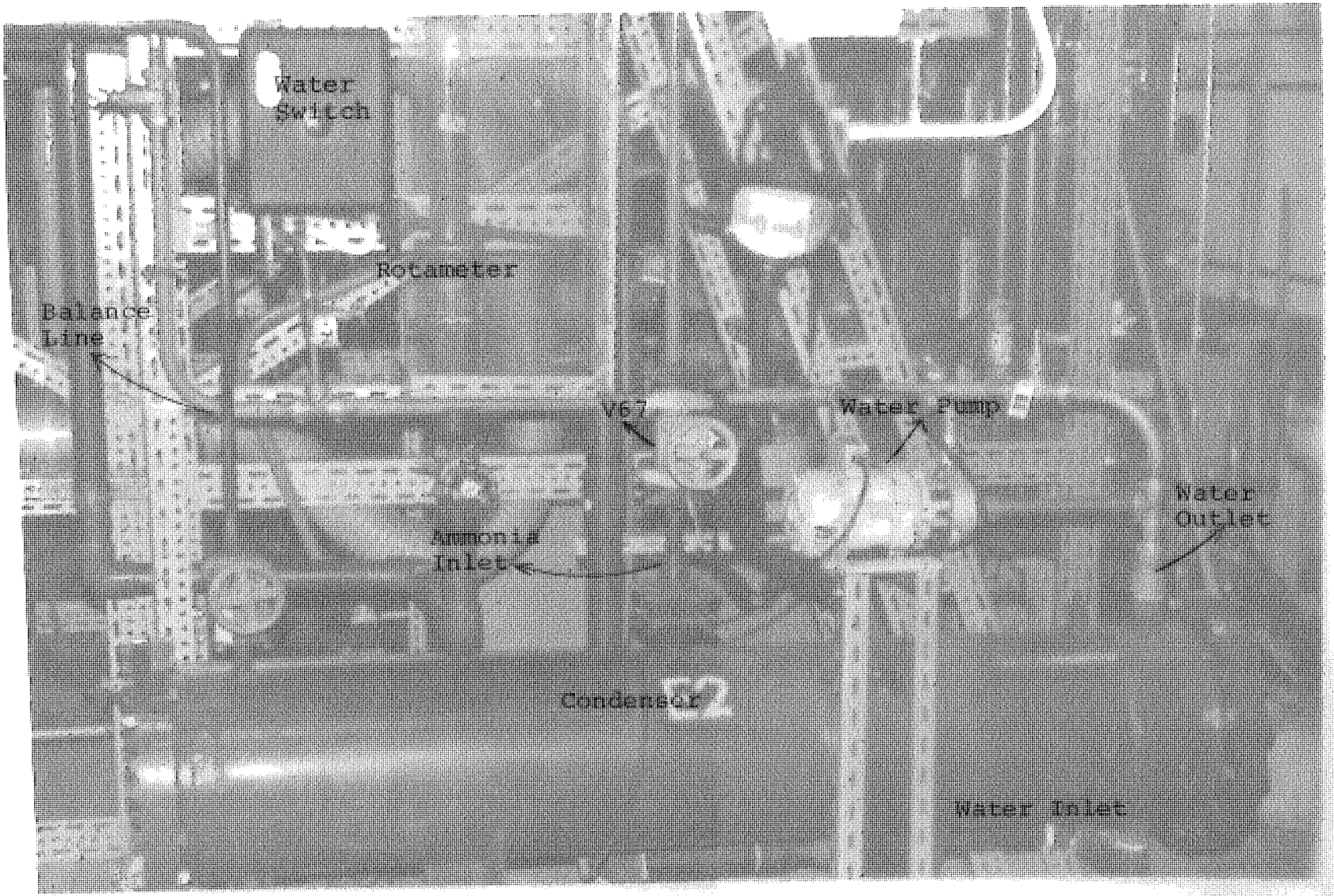
Figure 6.17.

THE COMPRESSOR WITH OIL SEPARATOR

Driven by a 10 h.p. 3 phase motor

Figure 6.18.

AMMONIA CONDENSER



The condenser had a condensing capacity of 22.27 kJ/s. (76.000 Btu/h.) based on a liquid ammonia flowrate of 90 litres/h. The specification of the condenser is given in Appendix 5C.

Superheated ammonia from the compressor entered the top of the condenser via V67 and subcooled ammonia left at the bottom via V69. A balance line was provided between the condenser and vessel S4; valve V85 served to adjust the pressure difference and hence to control the ammonia flowrate into the liquid receiver, i.e. vessel S4.

The condenser was provided with a pressure relief valve, set to relieve at 20.7 bar pressure.

Evaporator and Condenser Water Supply

Water from evaporator and the condenser recirculated to supply the latent heat of ammonia in the evaporator and to condense the gaseous ammonia in the condenser. The pilot plant cooling water passed through the condenser and then the evaporator. During extraction runs, water flowrate was increased by an external Stuart Turner pump with a capacity of 1000-500 gallons per hour. Water entered the condenser via a rotameter at the bottom. and was then fed to the evaporator. From the bottom of the evaporator it was returned to the cooling water supply tank.

A water flow switch in the inlet line to the condenser served to cut off the compressor and all the pumps in case of failure of the main water pump. The

relevant electrical circuit is shown in Appendix 4.

Following extraction runs water circulation was maintained to prevent frosting until the evaporator pressure increased and the condenser pressure decreased to the vapour pressure of ammonia at ambient temperature.

6.3. Commissioning of the Plant

The plant was commissioned in two parts; 1) commissioning of the extraction unit, including the R.D.C., settlers and storage vessels and, 2) commissioning of the solvent recovery unit.

6.3.1. The Extraction Unit

Commissioning of the extraction unit involved pressure testing, cleaning and operation in the absence of mass transfer.

Pressure Testing

Each storage vessel and settler was hydraulically pressure tested at 20.7 bar, and stamped, before installation. After installation initial pneumatic testing was carried out at 6.2 bar pressure and leaks were detected using soap solution. However, this method was not sufficient and therefore a gas detector (Leak Seeker Type TC,AI), with the system pressurised with carbon-dioxide, and later mass spectrometer with the system pressurised with helium, were used. Finally, owing to

the difficulties of detecting very small leaks the system was pressurised with Freon 22 at 10.3 bar pressure and a flame detector was used to search for them.

Pressure testing in this way demonstrated the need to replace some welded joints by compression couplings and to re-adjust the mechanical seal on the R.D.C. shaft.

Cleaning Procedure

Each storage vessel, settler and the R.D.C. was first washed with water to flush any residual scale or contaminants from the system. The water contained about 1% aqueous ammonia solution to give an alkaline pH and hence minimise corrosion of mild steel components. Water was drained from the lowest points of the pipe lines and via the drain lines from the tanks. Compressed air was blown through each tank with the drain valves open to flush water out of the system. Finally vacuum was applied to extract any residual moisture from the pipe lines and tanks.

Non-mass Transfer Experiments

Before introducing hydrocarbons and ammonia into the plant non-mass transfer experiments were carried out using kerosine and water. Kerosine was fed into S4 via V30, V28, V27, V31 with pump P1 operating; water was fed into S2 from V9. These experiments served to commission the pumps and to provide experience in controlling the flowrates of kerosine and water, maintaining the operating

pressure and the liquid interface in settler vessel S6 at a constant level by adjusting the heavy phase outlet flow into a container and the light phase flow into S1 via V49, V50 and V53. During these runs kerosine, the light phase, entered the R.D.C. at the bottom via V25, CV1, V45 with P1 operating; water entered either in the middle via V11, CV2, V13, V14 and V15 with pump P2 operating (R.O.) or at the top via V18, CV3, V24 with pump P3 operating (N.O.).

An operating procedure for use with ammonia-hydrocarbons systems was developed on the basis of these non-mass transfer experiments.

Subsequently, the R.D.C., settler vessel S6, storage vessels and connecting pipe lines were rinsed with water and blown through with compressed air after draining. The system was then evacuated for moisture removal. Pressure testing was repeated with nitrogen since some diaphragms of the stop valves required replacement following rupture under vacuum.

6.3.2. The Solvent Recovery Unit

Pressure Testing

The solvent recovery unit was first tested with nitrogen at 13.8 bar and soap solution. Small leaks were detected by pressurising the unit with Freon 22 at 10.3 bar pressure and using a flame detector. The

nitrogen, and subsequently Freon 22 cylinders were connected to the purging point on the delivery line of the compressor. Once the system was charged with ammonia leaks were found using a lighted sulphur stick,which produces smoke when held near an ammonia leak.

Charging the Solvent Recovery Unit with Ammonia

Ammonia was charged into the unit via an inlet point at the low pressure side. Before charging, the unit was evacuated using a 0.5 h.p., portable vacuum pump operated for 24 hours to dry out the system. The vacuum was first broken by gaseous ammonia supplied from a 29 kg. cylinder connected to the charging point on the inlet of the evaporator. Liquid ammonia was allowed to fill the system by pressure difference with the compressor operating. The evaporator pressure was 1 to 2 bar. compared with the ammonia cylinder pressure of 7.8 bar at 18^{o}C ambient temperature. The total charge was approximately 250 litres and this was stored in the evaporator and the condenser. Storage vessel S4 was charged with an additional 20 litres of liquid ammonia. Details of charging are given in Appendix 5D.

Operation

Before pumping solvent and feed into the R.D.C., the solvent recovery unit cycle was operated for 20 to 30 minutes until the evaporating temperature and pressure, and the compressor delivery pressure and temperature remained steady.

Table 6.5.

OPERATING PROCEDURE FOR THE SOLVENT RECOVERY UNIT

(Operations in sequence)

1.	Check that the crankcase heater is on and oil level is above 1/3 in the level gauge.
2.	Supply cooling water for compressor cylinder heads.
3.	Switch on condenser-evaporator circulating water pump.
4.	Check that V68, V63 are shut.
5.	Open valves in the following order: V55, V62, V66, V67, V69, V41, V25, V26, V58. (V84, V60 and V61 should always be open). V85 ¼ open.
6.	Switch on the compressor.
7.	Adjust the throttling valve (after at least 10 seconds compressor operated) to suction pressure between 1 to 3 bar indicated on the compressor suction pressure gauge.

The operating procedure for the solvent recovery unit is summarised in Table 6.5. and typical running conditions are given in Appendix 6. Temperatures were measured by a dial thermocouple unit.

6.3.3. Operability Studies

In design of the extraction plant considerable attention was given to safety because of the high operating pressure and toxicity of ammonia. It was necessary to consider all unexpected events and possible consequences. A hazard and operability study was, hence, carried out to assess the hazard potential of mal-operation or mal-function of individual items of equipment.

The operability study was performed at the commissioning stage; based on this study modifications were made to prevent hazards likely to arise from unexpected methods of operation under exceptional conditions. The study involved detailed questioning of the operation of every part of the equipment to discover how deviations could occur from the design intentions. The storage vessels, settlers, the R.D.C. and components of the solvent recovery unit were considered individually as were all interconnecting pipelines. The modifications introduced were e.g. additional pipelines, stop valves, non-return valves and pressure gauges. Detailed operating procedures were also devised. An example of the application of the hazard and operability study is given in Appendix 7.

6.3.4. Safety Aspects

Two emergency stop buttons connected to an alarm bell were provided, one in the fume cabinet, another near the entry to the pilot plant. These buttons were for operation if a major leak occurred and served to cut off the compressor, pumps, the R.D.C. drive motor, and to actuate a solenoid valve to supply water to the emergency spray.

In the case of minor leaks, amounting to no more than a tolerable smell of ammonia, a length of flexible P.V.C. hose was provided to spray water onto any pipe line within the fume cabinet. A safety warning for dealing with ammonia is given in Appendix 8.

Two people were always present during experiments. Safety gloves and face vizors were worn when working inside the cabinet. A Supervisor full face mask with a Vit-Air cannister Type H, and several cartridge respirators and goggles were provided ready for use. In case of a major leak, the emergency drill was for an approach to the leak to be made wearing a Supervisor full face mask with compressed air supply passing through a Sabre Filter-Pressure Regulator unit. A Sabre 'Escape Breathing Equipment', viz. a Supervisor full face mask and ½ hr. capacity air cylinder was also provided at the entry to the pilot plant.

6.4. Operating Procedure

Different operating procedures were devised for normal operation, (N.O.) and operation with reflux, (R.O.). This was necessary since in reflux operation feed was designed to enter at the middle of the column and different feed storage vessels, and pumps were used. The operating procedure involved a number of operations which are summarized below.

6.4.1. Normal Operation

Initial charging with the feed hydrocarbons pair was performed as described in Table 6.6. Hydrocarbons from 25 litre containers were pumped into S2 and mixed by re-circulation using pump P2 to obtain a homogeneous feed composition. A total of approximately 60 litres was charged and stored in S2 and S3.

To remove air from the system, evacuation of the R.D.C. and the top settler was performed before each extraction run using a vacuum line provided to the extraction plant. The procedure for evacuation is given in Table 6.7. The hydrocarbon mixture was subsequently fed into the system and pressurized to at least 7.8 bar pressure using the procedure listed in Table 6.8(a). Prior to extraction operation the solvent recovery unit was operated until temperatures and pressures reached steady values; this procedure is summarized in Table 6.5.

Table 6.6.

INITIAL CHARGING OF THE VESSELS WITH HYDROCARBONS

Operations followed strictly in sequence

Operating pressure = Atmosphere

1.	Connect P5 to S2 at feed charge point V9. (P5 Stuart Turner pump, 720/150 G.P.H., 10/45 Ft.Hd.).
2.	Open V8 (vent valve of S2).
3.	Check that V6, V10, V11 all shut.
4.	Pump known amounts of hydrocarbons to make the feed, (30 litres total approximately).
5.	Circulate the hydrocarbons around S2 for 30 mins via V11, V7, V6 with V9 and CV2 closed and P2 operating.
6.	Pump contents of S2 into S3 via V11, V7, V16 with V6, V4 shut and V20 open.
7.	Repeat operations 3, 4, 5.
8.	Shut V9, V16, V7, V11, disconnect P5 from feed charging point.

Table 6.7.

EVACUATION OF THE R.D.C., S6 AND CONNECTING PIPE LINES

Operations followed strictly in sequence

Operating pressure = 25 mm.Hg.

1.	Connect vacuum line to drain point of C1 at V44.
2.	Open valves, V13, V14, V15, V52, V47, V49, V5O, V45, V42, V53.
3.	Operate the vacuum pump.
4.	Stop vacuum pump when required vacuum (25 mm.Hg.) obtained.
5.	Shut valves V44, V13, V14, V15, V52, V47, V48, V49, V5O, V45, V42, V53.
6.	Separate vacuum line from V44.

Table 6.8(a)

HYDROCARBONS CHARGE INTO S6 AND THE R.D.C.

Operations followed strictly in sequence

Operating pressure = vacuum → 1O bar approximately.

1.	Open valves V11, CV2, V13, V14, V15.
2.	Crack open by-pass valve V12 and operate P2.
3.	Observe float in R2, monitor level increase in S6.
4.	Continue pumping until pressure in PI6 is about 1O bar.
5.	Stop P2 and shut V11, V12, CV2, V13, V14, V15. With this operation almost all contents of S2 i.e. about 3O litres, are transferred to fill and pressurise S6 and the R.D.C.

Table 6.9(a)

EXTRACTION PROCEDURE FOR NORMAL OPERATION

Operation followed strictly in sequence
Operating pressure: about 10 bar
Operation to be carried out simultaneously with solvent recovery unit running, i.e. Table 6.5.

1	Operate the solvent recovery unit Table 6.5. Start R.D.C. drive shaft motor, and water flow around mechanical seal.
2	Open valves V25, CV1, V45, crack open V52, partly close V58, operate P1. (In this operation ammonia is pumped into S6 and hydrocarbons leave the system via V52 into S1, to be replaced by ammonia with pressure maintained in S6 and the R.D.C. Pumping continued until ammonia is about mid-level in S6. Monitor level in sight glass of S6).
3	Open V18, CV3, V24, crack open V19, open V50, crack open V49, crack open V47, operate pump P3. (In this operation the feed is pumped to the top of the R.D.C. from S3 and, with operation 2 in progress, ammonia enters the R.D.C. at the bottom. Feed flowrate controlled by CV3 and V19, and ammonia flow-rate by CV1 and V26. Interface level controlled by adjusting V47 and V49, and the pressure maintained by controlling extract and raffinate flowrates by adjusting V52, V49). Continue extraction for at least 30 minutes.
4	Sample from SP1, SP2, SP3 at 10 minute intervals.

Extraction was carried out by pumping ammonia and the hydrocarbons simultaneously into the R.D.C; the extract flowed into the solvent recovery unit and the raffinate into S1. This involved control of both the pressure in the system and the interface level in the top settler. Samples were drawn from the sampling points, following the procedure used in the equilibrium studies (Section 5). The procedure for normal operation is given in Table 6.9(a). Operation lasted for 40-60 minutes; at the end of a run shut-down required the procedure given in Table 6.10.

6.4.2. Operation with Reflux

The procedure devised for operation with reflux is given in Table 6.9(b). The evacuation operation is as already summarized in Table 6.7; initial charging and pressurisation of the R.D.C. and the top settler with hydrocarbons is also similar to the procedure given in Table 6.8(a). However, in this case the contents of S3 are pumped for filling and pressurisation purposes (Table 6.8.(b); the contents of S2 are left in the vessel to be pumped during extraction. The procedure for this operation is given in Table 6.9(b). In reflux operation the feed is designed to enter the R.D.C. in the middle via pump P2 and reflux enters at the top via P3. Reflux is obtained by allowing hydrocarbons, from which ammonia has been removed in the evaporator, into S3 via V54.

Table 6.8(b)

HYDROCARBONS CHARGE INTO S6 AND THE R.D.C. (R.O.)

Operations followed strictly in sequence

Operating pressure = vacuum to 10 bar approximately.

1	Open valves V18, CV3, V24.
2	Crack open by-pass valve V19 and operate P3.
3	Observe float in R3, monitor level increase in S6.
4	Continue pumping until pressure in PI6 is about 10 bar.
5	Stop P3 and shut V18, CV3, V24, V19. Drain any hydrocarbons left in S3 via V17 to a storage can. Therefore, S3 will be empty for reflux collection from the evaporator.

Table 6.9(b)

EXTRACTION PROCEDURE FOR OPERATION WITH REFLUX

Operations followed strictly in sequence
Operating pressure = 10 bar approximately
Operation to be carried out simultaneously with solvent recovery unit, i.e. Table 6.5.

1	As '1' in Table 6.9(a).
2	As '2' in Table 6.9(a).
3	Open V11, CV2, V13, V14, V15, crack open V12, open V50, crack open V49, crack open V47, operate P2. (In this operation feed enters the R.D.C. in the middle. Operation is to be continued at least 20 minutes without reflux to collect hydrocarbons at the bottom of the evaporator for transfer to S3 via V54 to supply reflux).
4	Crack open V54, open V18, CV3, V24, crack open V19, operate pump P3. (In this operation reflux is fed to the R.D.C. at the top. The outlet valves for extract and raffinate flow 49, 42, to be opened slightly more to control the pressure within the system.)
5	Sample from SP1, SP2, SP3.
6	Continue operation for at least 30 minutes.
7	Shut-off procedure as listed in Table 6.10.

Table 6.10.

SHUT-OFF PROCEDURE

1	Stop P1, shut valves CV1, V45, stop P3, shut valves V18, V19, CV3, V24.
2	Stop R.D.C. drive shaft motor.
3	Open V48, to allow ammonia rich top layer to flow into evaporator; when interface level just below mid-level shut V42. When all ammonia rich phase transferred into evaporator, stop solvent recovery unit, shut valves V48, V49, V50.
4	Open V42 to transfer bottom layer into S1. If S1 full, open V4, V11 to transfer S1 contents into S2.
5	Finally vent S6 and the R.D.C. Carry out operations listed in Table 6.7. and 6.8. in preparation for next run.

At the end of a run all the pipe lines likely to retain liquid ammonia were vented from the nearest vent valve.

In the event of mal-operation or a leak during any of the procedures in the above Tables, emergency action was based upon the magnitude of the hazard. In generaly any operating part of the plant was first switched off e.g. pumps, drive shaft motor, compressor. If there was a leak, e.g. at a pipe joint, the line was isolated at the nearest valves. If ammonia was seaping out water was sprayed onto the joint from a hose.

7. Results

Experiments using kerosine and water in the absence of mass transfer were carried out using the operating procedures given in Tables 6.6. to 6.10. However, when ammonia was introduced into the system unexpected operating problems were experienced with some parts of the plant, e.g. pumps P1, P2, P3 and diaphragm valves. This necessitated some deviations from the planned operating procedure. The difficulties following the introduction of ammonia into the system and vacuum application were;

i) Evacuating the system by vacuum application for removal of air, as described in Table 6.7., shortened the life of the p.t.f.e. diaphragms of stop valves resulting in leakages. Vacuum application was therefore eliminated. The hydrocarbons were charged into the R.D.C. and the top settler with vent valve V51 open; when S6 was completely full the vent valve was closed and the system was then pressurised.

ii) Pump P1 developed a leakage of ammonia via the piston shaft. Since this could not be eliminated the pump was taken out of service. Ammonia was subsequently allowed to flow into the system from S4 at the delivery pressure of the compressor. This was no disadvantage apart from limiting the operating pressure to the delivery pressure of the compressor which varied between 8.6. and 9.7. bar.

iii) Although all the pumps were recommended for use with ammonia and hydrocarbons, the feed pump failed to work when the feed contained small amounts of ammonia (<1% volume) dissolved in hydrocarbons. This was attributed to cavitation as ammonia was converted into gas by suction of the piston. A gaseous ammonia purge line branching from the delivery line of the pump did not solve the problem. Therefore, countercurrent flow of feed and solvent was obtained in two different ways for the two systems as described below.

7.1. Results and Observations

7.1.1. System: Heptane-Cumene-Ammonia

Five experiments were carried out to extract cumene from a heptane-cumene feed. Countercurrent flow of the feed and solvent was considered to be obtained by allowing hydrocarbons to enter the R.D.C. from the top settler and flow downward by gravity with ammonia flowing upwards. The system was first charged with feed stock using a ¼ h.p. Stuart Turner pump with vent valve V51 open. Ammonia was then allowed to flow into the R.D.C. from vessel S4. When the pressure in the top settler was equalized with the pressure in S4, i.e. the compressor delivery pressure, the hydrocarbons mixture was allowed to flow via V47 downwards into the R.D.C. and raffinate was discharged into S1 via V42. The interface level in S6

dropped continuously as raffinate left the system. Experiments were continued for about 30 minutes and samples were withdrawn at about 10 minute intervals. When an experiment was completed, hydrocarbons were transferred from one storage vessel into another by draining it into a storage can; it was then pumped by the Stuart Turner pump for use as feed stock in the next experiment.

The experiments were carried out at 300 r.p.m. and 600 r.p.m. rotor speeds. The speeds were selected on the basis of preliminary trials with the system kerosine-water in which rotor speed was varied between 200 r.p.m. and 900 r.p.m. (the maximum obtainable). Also calculations based on interfacial tension and column geometry indicated a minimum speed of 225 r.p.m. and a maximum speed of 650 r.p.m.

The feed compositions approximated to 20%, 40% and 50% in order to cover a range of extraction operations on the triangular diagram (Figures 7.1. to 7.4.). The phase ratio could only be roughly determined within the operating range for an R.D.C. i.e., between 1 to 4 or 4 to 1. However, it could subsequently be determined accurately from the amount of raffinate collected in S1, compositions of extract and raffinate and solvent flowrate.

Hydrocarbons analysis and titration for determination of the amount of ammonia were performed as in the Equilibrium Studies. Calibration charts to relate integrator

values to volumetric compositions are included in Appendix 9A.

The column was operated for a time at least equivalent to a 2.5 times volumetric displacement before taking the first samples of extract and raffinate E1 and R1 respectively. Subsequently samples E2 and R2 were taken approximately 10 minutes later. The analytical data including chromatographic and titration results are given in Appendix 9B ; the compositions of the extract, raffinate and feed samples taken at time intervals are illustrated in Figures 7.1. to 7.3. The compositions of the extract and the raffinate exhibited some inconsistencies, with some samples of raffinate containing more ammonia than the approximate 10% predictable for extraction from the triangular diagram (Figure (5.7.)). This indicates that not all of the feed and the solvent flowed countercurrently in the column. In fact, only a portion of the ammonia rich phase was collected in the top settler with some leaving the storage vessel S1 with the raffinate. The results are discussed in Section 7.2.

7.1.2. System: Methylcyclohexane-Toluene-Ammonia

Using mixtures of methylcyclohexane and toluene as feed, 4 experiments were completed at different solvent to feed ratios and feed compositions. Fresh feed stock, i.e. ammonia-free, was used in each run so that the feed pump was operable. It was necessary to check the

diaphragms of stop valves at sampling points and extract, raffinate outlet lines between runs to avoid loss of samples; these valves were repeatedly tested pneumatically at 6.2. bar. The R.D.C. and top settler were initially charged with fresh hydrocarbons containing no ammonia as described in Table 6.8(a). All experiments were carried out at a rotor speed of approximately 300 r.p.m. Analyses were performed in a similar manner to those for the system heptane-cumene and ammonia. Calibration charts to relate integrator readings to volume percentages are given in Appendix 10A. Tie line data which was obtained from the literature (35), is represented in Appendix 10B.

7.1.3. Solvent Recovery Unit Performance

The solvent recovery unit was operated by the procedure in Table 6.5. Temperatures and pressures at the inlets and outlets of the evaporator, condenser and compressor were recorded. The unit was operated until steady temperatures and pressures were obtained before starting an extraction run.

The compressor suction and delivery pressures were controlled by adjusting the throttle valve on the ammonia inlet line to the evaporator. In practice operation with this valve 20% open gave the desired operating conditions i.e. without the low suction pressure or high delivery pressure cutouts being actuated. The operating conditions for the solvent recovery unit during Experiment 2 are

summarised in Appendix 6. During an experiment frost tended to build up on the ammonia inlet line to the evaporator beyond the throttle valve. This was due to the pressure drop across the valve resulting in flashing of liquid ammonia and hence low temperatures. However, this did not affect operation of the unit.

7.2. Discussion of Results

A total of 9 runs was completed involving the extraction of aromatics using two different hydrocarbon systems. A different method of operation was used for each system.

The extraction plant and the solvent recovery unit operated satisfactorily, and safely, in accordance with the standard operating procedures with the system, Toluene-Methylcyclohexane-Ammonia. Satisfactory extraction was obtained in the R.D.C. at a rotor speed of 300 r.p.m. and different solvent to feed ratios, and feed compositions. A number of design improvements arising from the commissioning trials and experimental runs are discussed in Section 8.

System: Cumene-n.Heptane-Ammonia

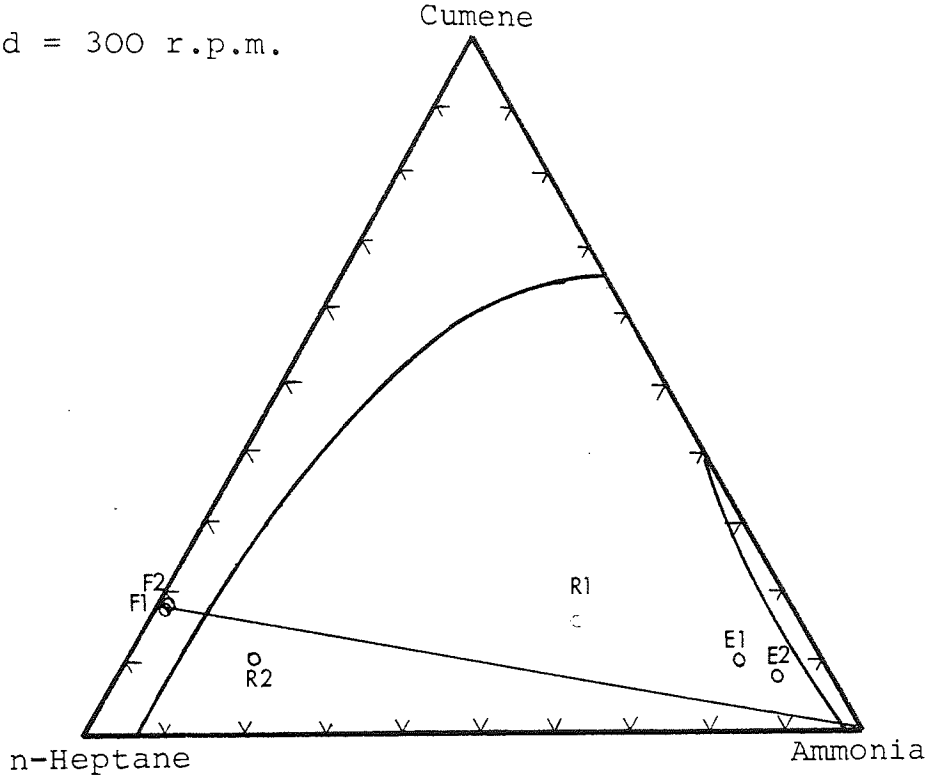
The equilibrium data for this system is discussed in Section 5.4. It is a Type 2 system and therefore should be ideal for reflux application, (Section 2.2.1.) and will enable an extract of unlimited purity to be obtained. It presented no problems in use i.e. a clear interface was obtained without scum formation. However, unlike glass laboratory columns (57, 58) it was not possible to observe flow within the column.

The experimental results obtained with this system, as shown in Figures 7.1. to 7.3., exhibit some inconsistencies

Figure 7.1.

EXTRACTION WITH FEED CONTAINING <20% (vol) CUMENE

Rotor Speed = 300 r.p.m.



Rotor Speed = 600 r.p.m.

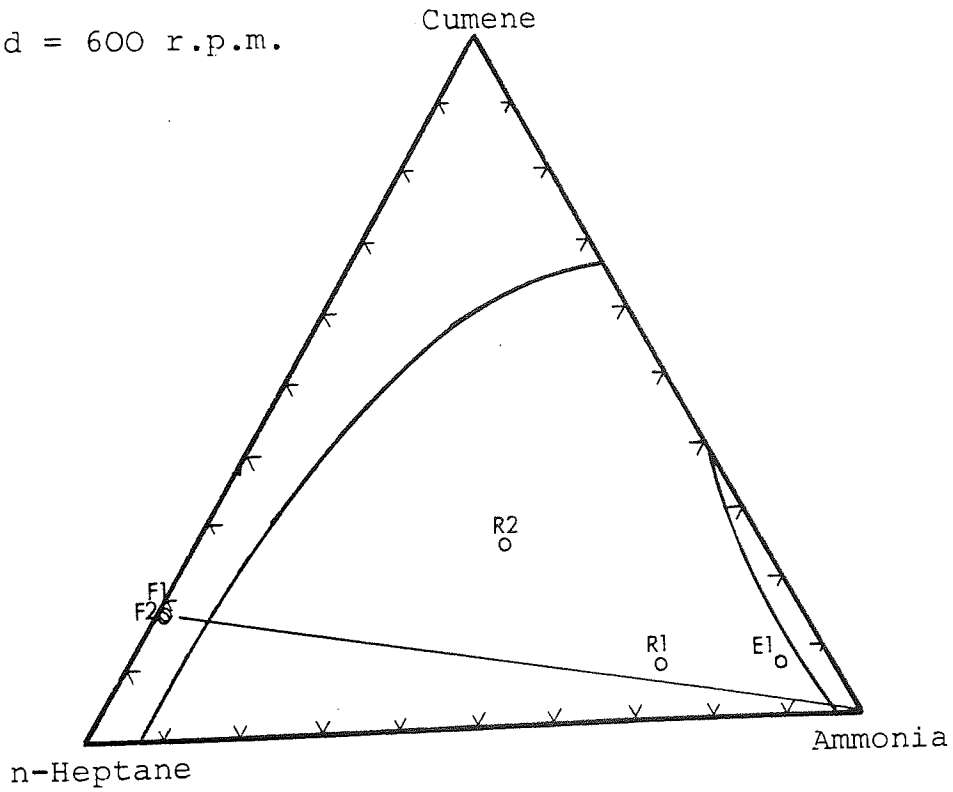
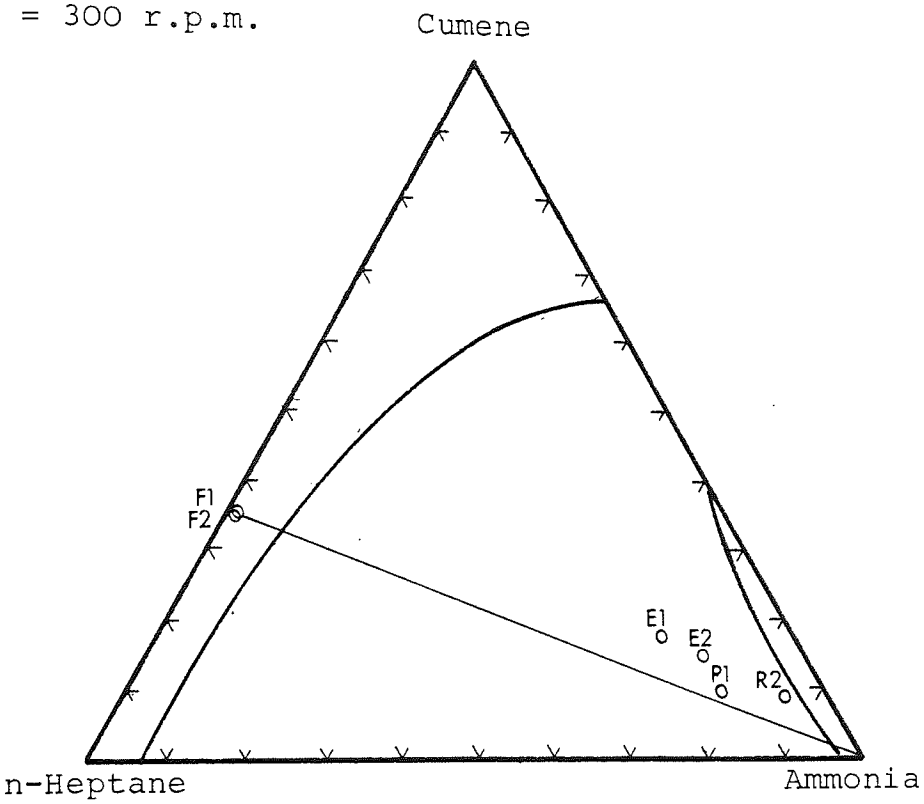


Figure 7.2.

EXTRACTION WITH FEED CONTAINING <40% (vol) CUMENE

otor Speed = 300 r.p.m.



otor Speed = 600 r.p.m.

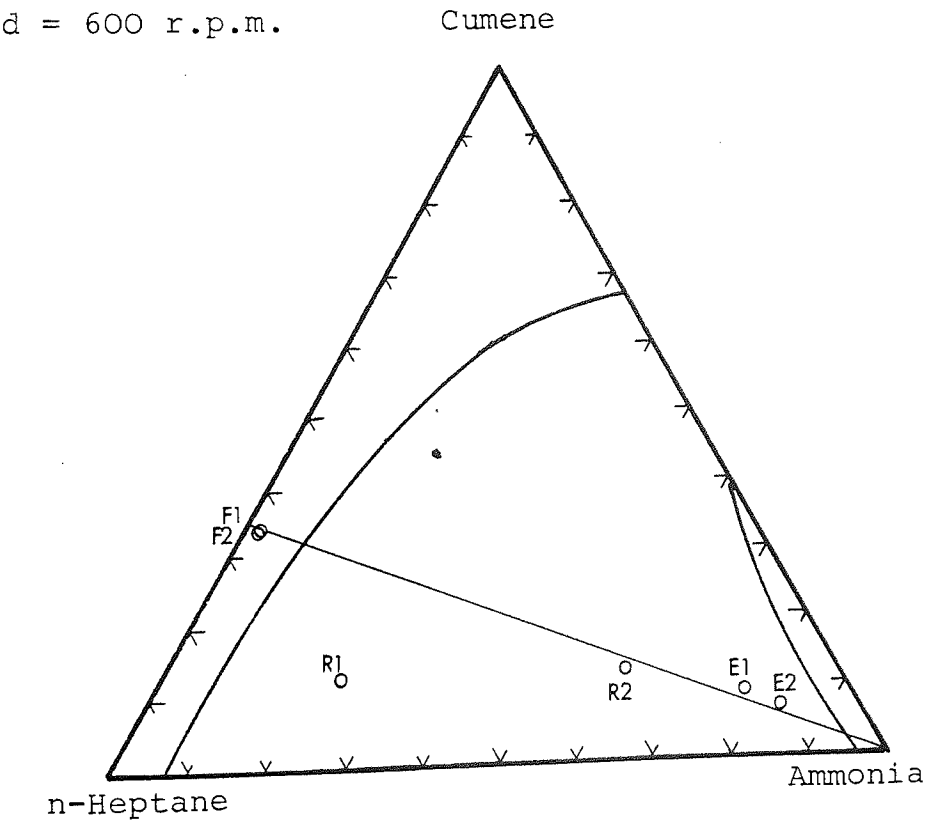
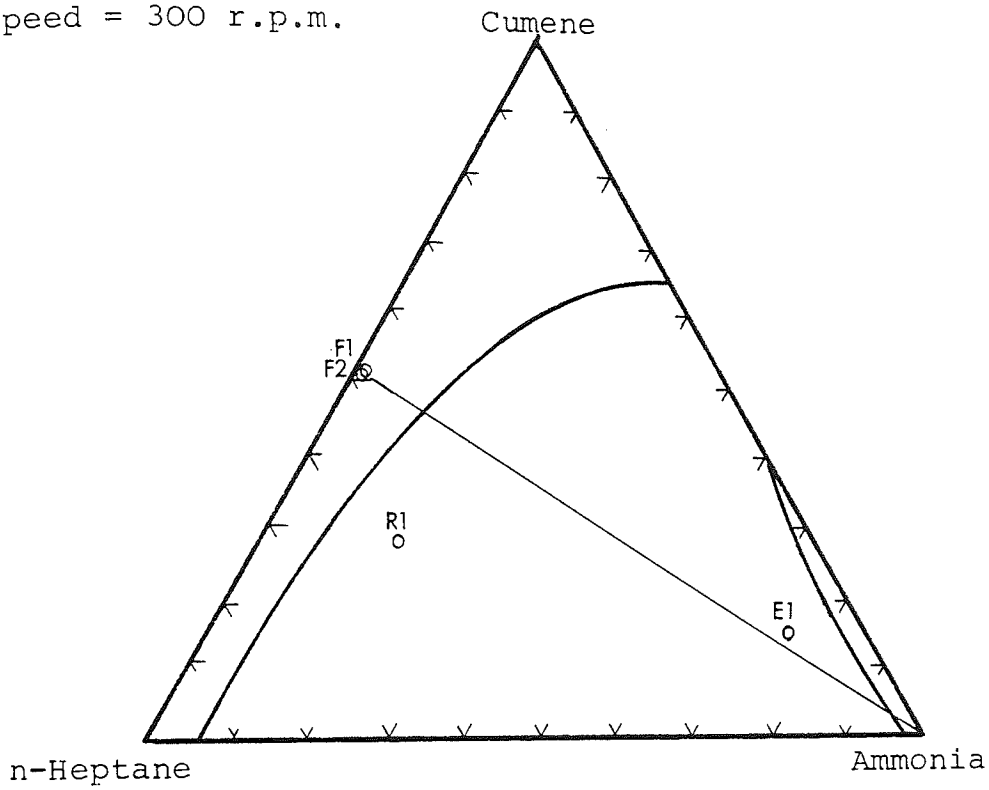


Figure 7.3.

EXTRACTION WITH FEED CONTAINING >50% CUMENE

Rotor Speed = 300 r.p.m.



in raffinate compositions and, to some extent, in extract compositions. Some raffinate samples contained high concentrations of ammonia and higher percentages of cumene than that present in the feed. This indicates (a) that there was poor separation between raffinate and extract and/or (b) countercurrent flow was not maintained throughout the column. Since a satisfactory density difference (e.g. $>0.05 g/cm^3$) is required between the contacting phases in a continuous countercurrent column, one explanation for (a) could have been a twin density condition. In these circumstances the two liquid phases in contact have identical densities (119) at some point in the column which results in poor separation of the phases. Hence, densities of the raffinate and extract phases were tabulated with the ordinate as solute concentration as shown in Figure 7.8. This demonstrates, however, that the raffinate densities were always higher than the extract phase densities; therefore a twin density condition could not occur within the column. The excessive amounts of ammonia in the raffinate may have been caused by ammonia which entered at the bottom of the R.D.C. tending to flow straight into raffinate storage vessel S1 without travelling along the column due to differential pressure. Prior to extraction the top settler and the R.D.C. containing hydrocarbon mixture were pressurised by ammonia from vessel S4. When the pressures in the system and vessel S4 equalised, ammonia flow ceased and extraction was

then carried out by cracking open valve V42 for the removal of hydrocarbons as raffinate phase into S1, thus allowing more ammonia into the R.D.C. to replace the hydrocarbons. However, when V42 was cracked open and as some ammonia flowed upward in the column, some may have left with raffinate to S1. Hence, the required proportions of continuous countercurrent flow of feed and solvent in the column may not have been achieved. Unfortunately, because of the constraints imposed by the operating pressure, no visible flow sections could be built into the column to check the phase flows. Nevertheless, extract compositions showed that extraction took place and larger percentages of cumene were obtained in the extract phase. The experimental results were rather inconclusive; to improve upon them with this system would involve either replacement of the pumps by a self-priming type or use of fresh, i.e. absolutely ammonia-free, feed stock so that the feed pump would operate without cavitation.

System: Toluene-Methylcyclohexane-Ammonia

This is a Type 1 system and the equilibrium data was obtained from the literature (35) at 21.1^{o}C. For best use of reflux the system would need to be converted into a Type 2 system either by reduction of extraction temperature (Figure 3.6.) or by use of an antisolvent e.g. water (Figure 3.10.).

With this system the results obtained for normal, i.e. non-reflux operation, at different solvent to feed ratios and feed compositions, are shown in Figures 7.4. to 7.7. Prior to extraction the system was pressurised with the hydrocarbons to at least 8.3. bar. Ammonia was then allowed to enter the R.D.C. in liquid form and feed was pumped in with the extract and raffinate valves, V49, V42,cracked open to maintain the pressure and the interface in the top settler. Before samples were withdrawn the pipe lines to the sampling pot were drained to ensure that only representative samples of raffinate or extract entered it.

The analysis of the samples taken at time intervals showed a reasonable agreement, mostly within 2%. However, some of the extract and raffinate compositions obtained were slightly outside the equilibrium curve. This was due to slightly lower temperatures in the R.D.C., i.e. 18^{o}C to 20^{o}C, compared with the temperature at which the equilibrium curve was obtained (21.1^{o}C equilibrium temperature).

A comparison was made between the experimental results and those predicted from theory, using the mass transfer relationships developed for the R.D.C. (Section 4). From Equation 2.1. the amount of toluene transferred was calculated using estimated values for the mass transfer area, mean driving force and overall mass transfer coefficient. From the calculated toluene transfer and

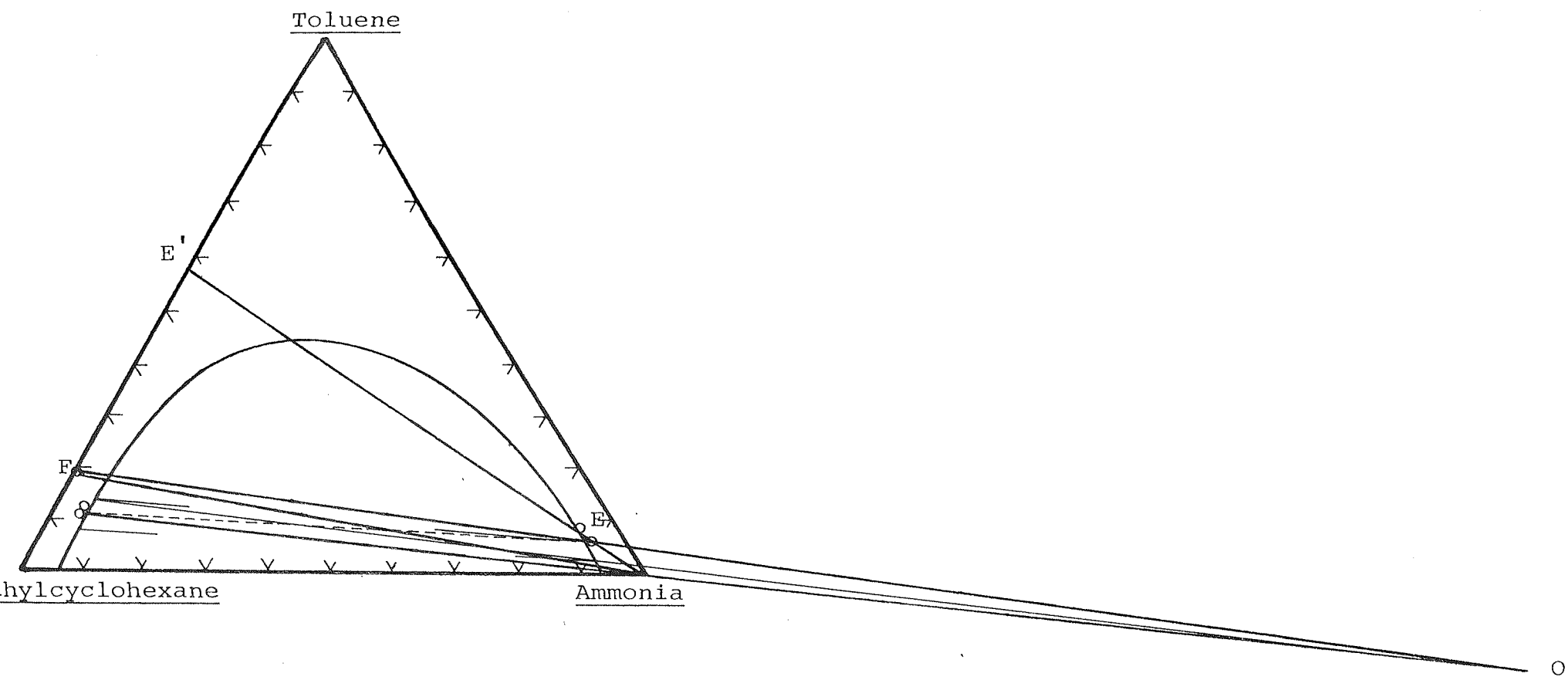


Figure 7.4.

(EXTRACTION AT 300 r.p.m.; S/F=1., S = F = 0.25 l/min.

FEED COMPOSITION: 19% Toluene,81% Methylcyclohexane)

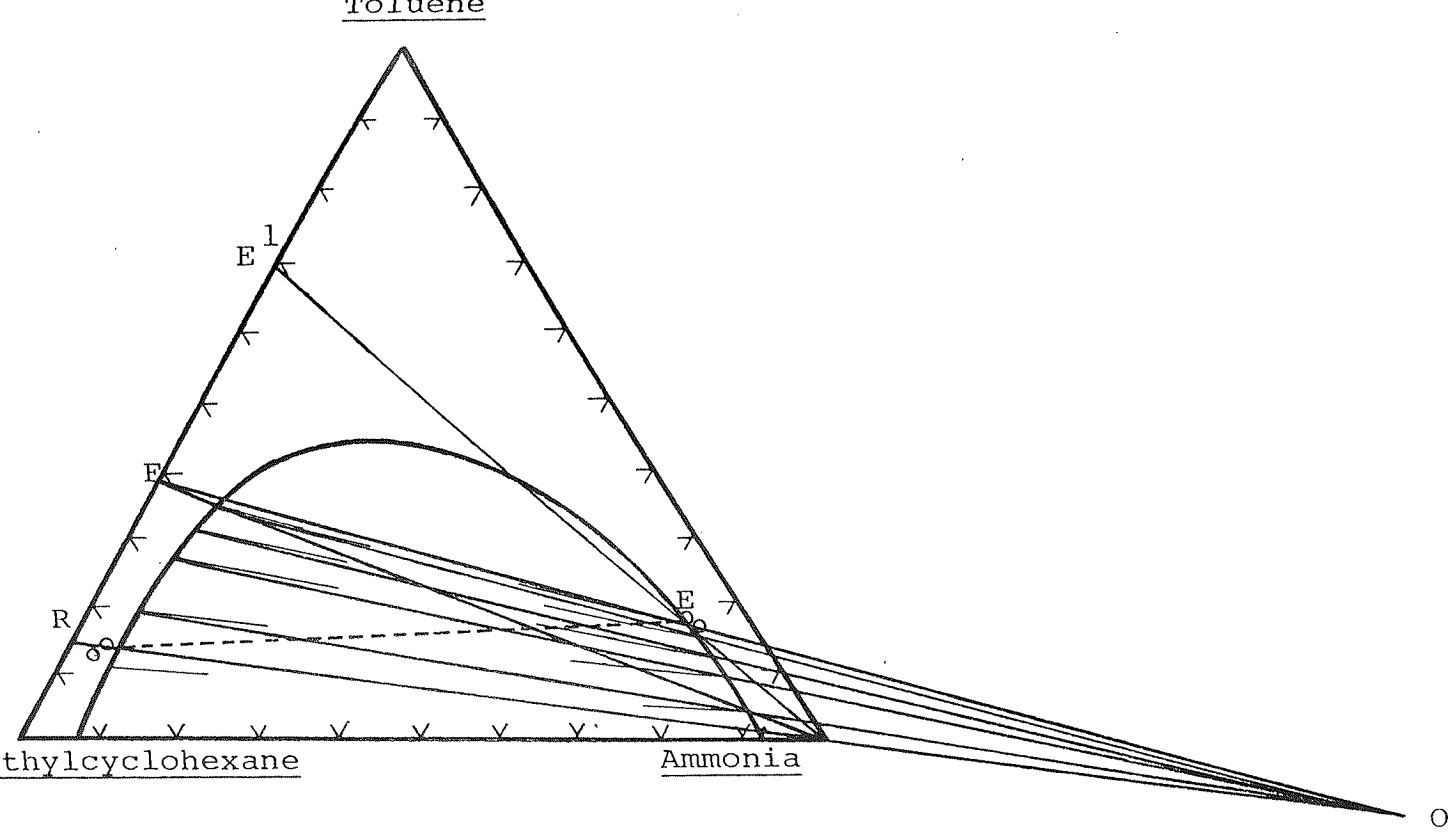


Figure 7.5.

(EXTRACTION AT 300 r.p.m.; S/F = 1 , S = F = 0.25 l/min.

FEED COMPOSITION: 39.5% TOLUENE, 60.5% METHYLCYLOHEXANE)

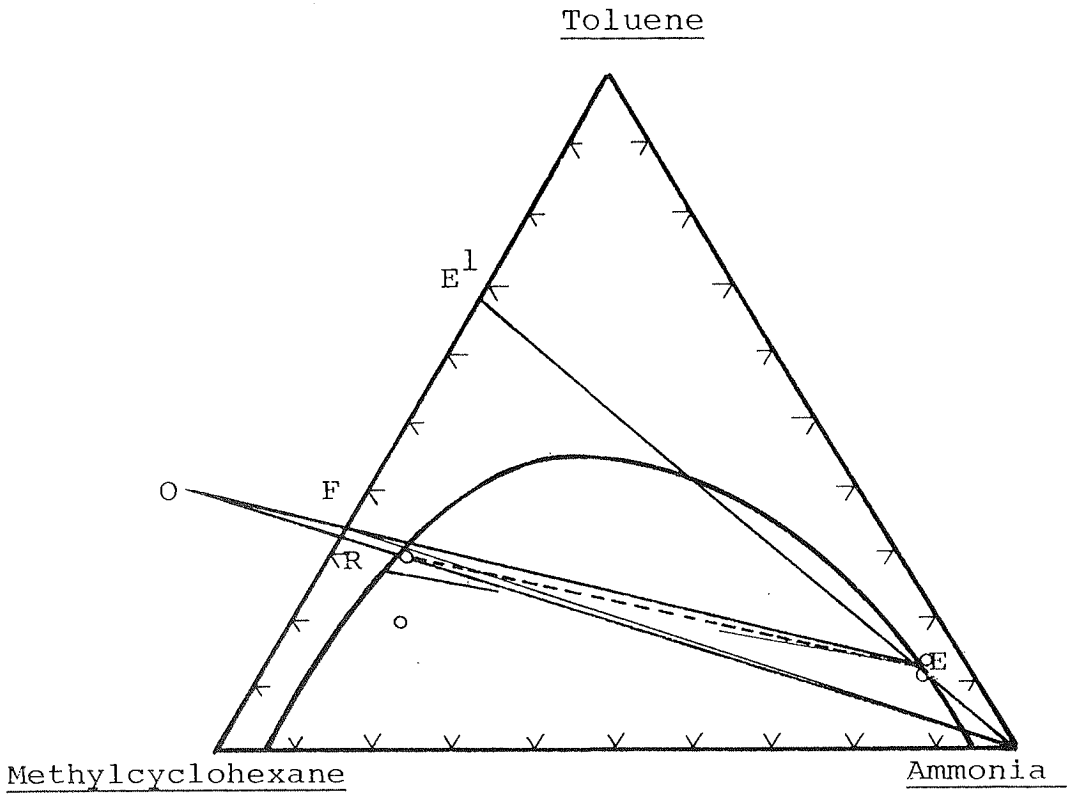


Figure 7.6.

(EXTRACTION AT 300 r.p.m., S/F = 1/5, S = 0.15 l/min., F = 0.75 l/min.,

FEED COMPOSITION: 34.5% Toluene, 65.6% Methylcyclohexane).

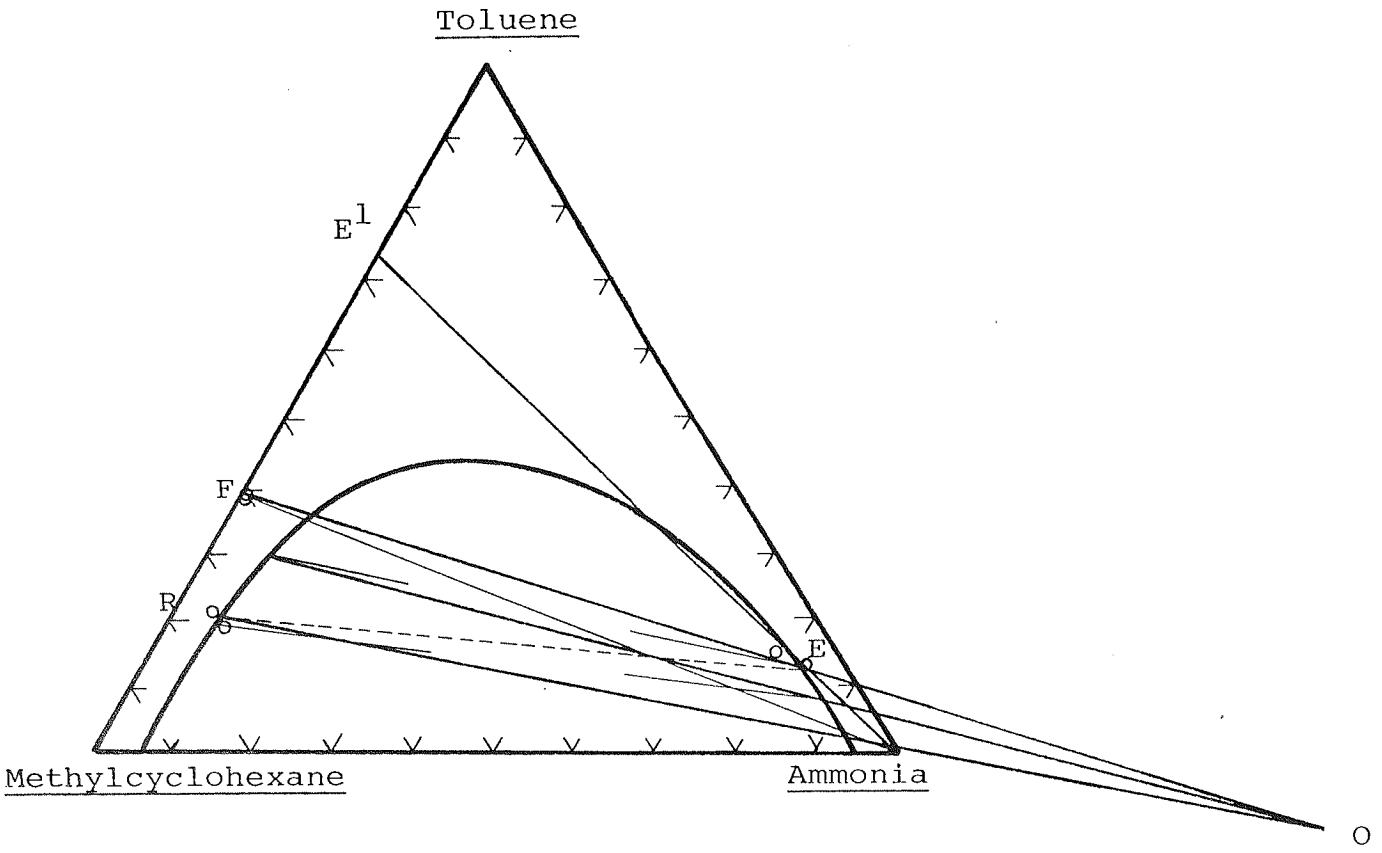


Figure 7.7.

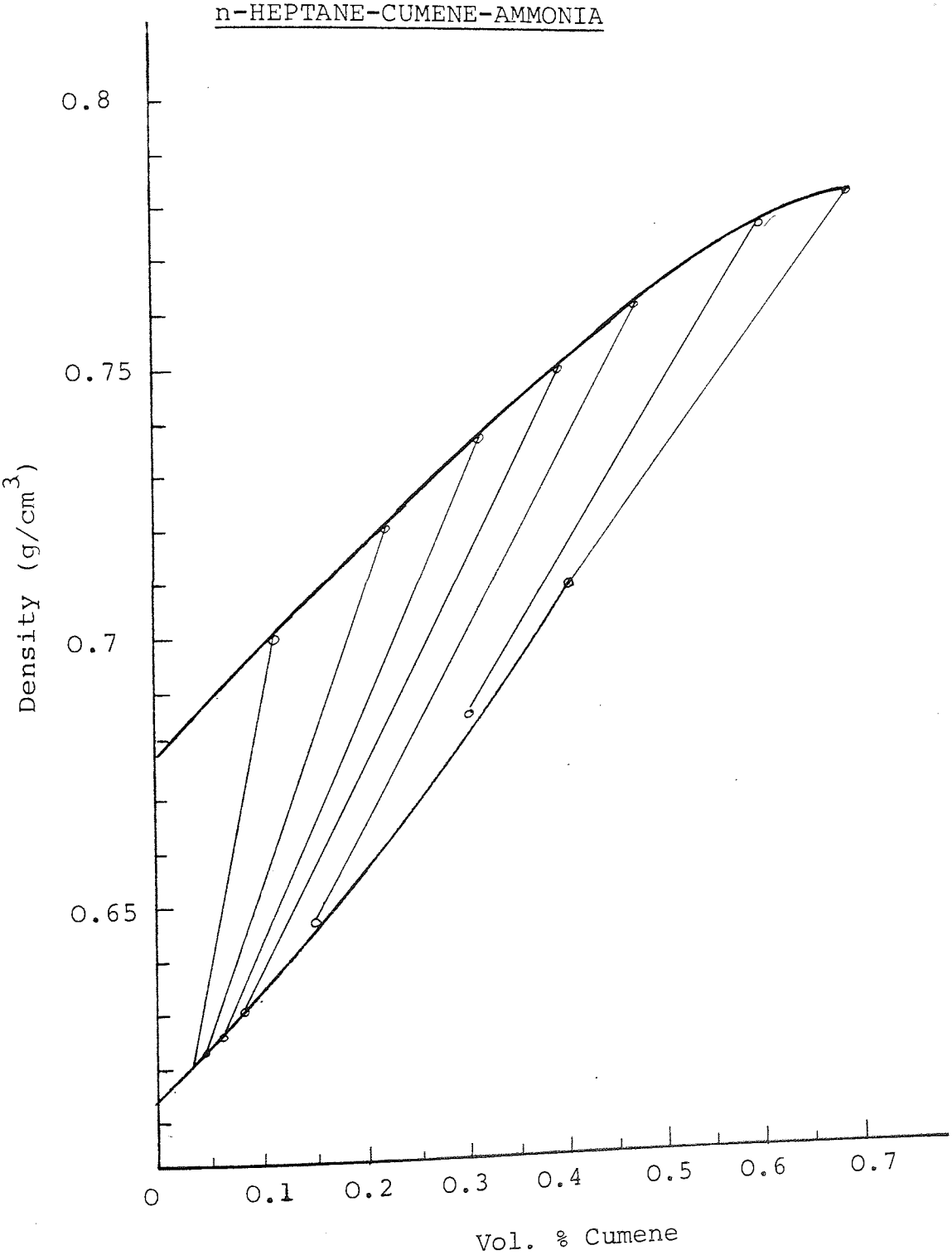
(EXTRACTION AT 300 r.p.m., S/F = 2/1, S = 0.4 l/min., F = 0.2 l/min.,

FEED COMPOSITION: 39.5% Toluene, 60.5% Methylcyclohexane).

Figure 7.8.

DENSITIES OF EQUILIBRIUM PHASES IN SYSTEM:

n-HEPTANE-CUMENE-AMMONIA



No tie line exhibits a reversal sign - hence a twin-density condition cannot occur.

compositions of extract and raffinate phases, extract and raffinate rates were found and E + R was compared with experimental F + S values.

Since it was impracticable to observe the drops in the column, drop sizes were calculated using two relationships, one developed by Kolomogoroff (Equation 4.29) and the other proposed by Misek for the laminar

$$d = 0.38\left(\frac{\gamma}{\Delta\rho . g}\right)^{0.5}$$

region ($Re << 10^4$) by analogy with the break-up mechanism in a packed column. Drop sizes calculated from this equation were less than 1mm.; such drops would be stagnant. Alternatively, Equation 4.29 predicted drop sizes above 2mm. diameter and these are assumed to be circulating. Since the real situation was not known, mass transfer calculations were carried out for either case.

The surface area for mass transfer was calculated from the drop size and hold-up values. Mass transfer coefficients for continuous and dispersed phases respectively were estimated using Strand's recommendation (112) for stagnant drops,

$$k_c = 0.001\bar{V}_N(1-X)$$

$$k_d = \frac{2\pi^2 D_{AB}}{3d_o}$$

For circulating drops mass transfer coefficients were

related to diffusivity of the continuous phase by Strand's equation (112) for k_c and Kronig and Brink's (113) suggestion for k_d respectively.

$$k_c = \frac{\sqrt{4\bar{V}_N D}}{d_o}$$

$$k_d = \frac{17.9\ D}{d_o}$$

For the approximate estimation of diffusivity the following equation was used (112) with the association factor Φ for solvent-ammonia assumed as 1.

$$D = \frac{7.4(10^8)(\Phi M_B)^{0.5} T}{\mu \cdot V_A^{0.6}}$$

Finally, the mean driving force was calculated using Simpson's rule from the distribution co-ordinates. An example of the calculation is given in Appendix 11 and results for all experiments are listed in Table 7.1.

Calculated mass transfer values compared reasonably well with experimental results, i.e. within 20% assuming either stagnant or circulating drops. This meant that relationships developed for larger diameter R.D.C.'s could be applicable to the 5cm. diameter R.D.C. This agreement probably arises since because the distribution of drops present comprise a mixture of stagnant and circulating drops.

Table 7.1.

MASS TRANSFER RATE CALCULATION

For circulating drops

	EX1	EX2	EX3	EX4
(cm/sec)	0.2122	0.2122	0.1273	0.3397
"	0.2122	0.2122	0.6366	0.1698
"	6.34	7.083	7.083	7.083
	0.6314	0.6266	0.6266	0.6266
	0.97	0.98	0.98	0.98
	63.873	69.804	69.804	69.804
	0.418	0.441	0.3508	0.3827
(cm)	0.217	0.223	0.223	0.223
	147279	143174	113631	125221
(cm^2)	21787.7	22368.1	17752.4	19563.2
(cm/s)	0.0651	0.0678	0.0678	0.0678
"	0.0011	0.0011	0.0011	0.0011
"	0.0012	0.0012	0.0012	2.3
	2.3	2.3	2.3	0.0012
	0.02075	0.03725	0.0525	0.03975
(cm^3/min)	31.29	60.58	68.16	57.28
"	134.	263.	605.	197.45
"	481.	346.	470.	409.14
+ E "	615.	609.	1075.	606.692
+ S "	500.	500.	900.	600.00

For stagnant drops

	EX1	EX2	EX3	EX4
d_o (cm)	0.0773	0.082	0.082	0.082
	0.8164	0.8046	0.8046	0.8046
	0.85	0.86	0.86	0.86
e		25.67	25.67	25.67
	0.448	0.47	0.375	0.416
(cm^2)	65523.8	64830.7	51726.4	57381.8
V_c (cm/sec)	0.00055	0.00375	0.00375	0.00375
V_d "	0.00109	0.00185	0.00185	0.00185
"	0.00025	0.00066	0.00066	0.00066
(cm^3/min)	20.15	95.42	108.03	91.3
"	225.	22.	478.	-
"	310.	545.	745.	-
+ E "	535.	567.	1223.	-
+ S "	500.	500.	900.	-

Temperatures and pressures in the solvent recovery unit during experiments were recorded and a typical running condition is included in Appendix 6.

Viscosity and surface tension of hydrocarbons required for the mass transfer calculations were measured using Cannon-Fenske viscometer Type BS/lP/CF and White Torsion Balance for surface tension measurements at $20^{o}C$. The tie line data for this system is given in Appendix 10B.

8. Conclusions

1. Despite its toxicity and the need for operation under pressure, liquid ammonia appears to be a useful solvent for the separation of aromatic hydrocarbons from non-aromatic constituents.

Its ease of recovery makes it feasible to apply reflux, and hence obtain a purer extract, in those systems exhibiting Type 2 equilibria.

2. The 5cm. internal diameter, 50 compartment R.D.C. and ancilliaries, operating at 10 bar pressure, and the solvent recovery unit designed as part of this work (Section 6) proved satisfactory in most respects.

The technique of a Hazard and Operability Study (Section 6.3.3.) was most useful in indicating the need for minor modifications, in devising operating procedures (Section 6.4.) and in confirming that the plant was safe to operate.

With the system Toluene-Methylcyclohexane-Ammonia both the extraction plant and the solvent recovery facility operated satisfactorily, and safely, in accordance with the operating procedures.

Experimental results gave reasonable agreement with extraction performance predicted from drop size, hold-up and mass transfer relationships for the R.D.C.

3. The equilibrium bomb designed and used in this study to determine liquid-liquid equilibria for Cumene-

n-Heptane-Ammonia under a pressure of about 10.3 bar worked well (Section 5.). The data are typical of a Type 2 system. The techniques for sampling under pressure and analysis developed for this purpose were later used satisfactorily in the extraction experiments.

Clearly, the bomb and techniques are of general application to other liquid-liquid systems under pressures not exceeding 20.6 bar pressure.

4. The safety equipment provided for the extraction plant, the personal protection measures, and the procedures developed to ensure safe operation, functioned satisfactorily.

5. This study has taken the design and operation of the R.D.C., ancilliaries and solvent recovery unit to a stage at which further extraction runs (either with or without reflux) can be performed with selected systems to compare the suitability of ammonia with other solvents. Practical recommendations relating to this are given in Section 9.

9. Recommendations for Further Work

The following areas of further work are recommended.

Equilibrium Studies

The equilibrium bomb designed and operated in this study can be used to determine liquid-liquid equilibrium data for any ternary system at high pressure. To allow data to be obtained at a higher temperature than ambient temperature, provision was made for circulation of heat transfer medium e.g. hot or chilled water through a jacket.

Use of Extraction Plant

Further work can certainly be performed with ammonia in the existing extraction plant using the procedures outlined in Section 6.4. However, due to difficulties in pumping hydrocarbons contaminated with small amounts of ammonia as feed into the R.D.C., the feed pump would require replacement by a reliable self-priming pump. (Alternatively, fresh feed stock would need to be used in each experiment). Any new pump should also be more suitable for consistent operation at low capacities, i.e. 0.1-1.5 l/min. Although each of the existing pumps was specified for low capacities, piston pulsation resulted in some fluctuations in flowrate. This could be overcome by absorbing the pulsations in an external pipe system but this may need to be of considerable length; therefore a damper cell may be needed. The existing pumps could be serviceable if the pressure at the suction side was maintained above 7.9 bar to ensure that the

pressure above any ammonia dissolved in the hydrocarbons was well above its appropriate partial pressure at ambient temperature; hence the ammonia would remain in liquid form. However, this method could result in further complications, e.g. associated with the use and subsequent venting of nitrogen. It will also be necessary to replace any diaphragm valve in a position where vacuum must be applied; the preferred replacement would be a needle valve constructed to close tolerances with stainless steel seat for good sealing.

The extraction plant could be used to separate any other hydrocarbon mixed feed with ammonia as solvent. Some hydrocarbons which could be used are listed in Appendix 2.

Furthermore, reflux can be applied using the proposed operating procedure given in Table 6.9(a). A hydrocarbon mixture which produces a Type 2 system with ammonia at ambient temperature would be most suitable for use with reflux and would enable column performance at different reflux ratios to be investigated. The system for which experimental equilibrium data were obtained (Section 5) was a Type 2 system and hence suitable.

The extraction plant was also designed to enable ammonia to be used with a modifying agent to change the hydrocarbon's solubilities in ammonia. Either water, as anti-solvent, or monomethylamine, as pro-solvent, can be used to alter the solubilities of paraffinic and

aromatic hydrocarbons. Toluene-methycyclohexane-ammonia gives a Type 1 system at ambient temperature but a Type 2 system could be obtained by addition of small amounts of water to the ammonia; therefore reflux application could be performed to obtain an extract containing above 75% volume toluene on a solvent-free basis. Alternatively, extraction could be carried out at a lower temperature than ambient by construction of a jacket on the R.D.C. and circulation of a refrigerant. A lower temperature will 'open-up' the equilibrium curve and hence a Type 1 system could be converted to a Type 2 system. Extraction at a different temperature, or extraction with modified solvents would involve revision of the operation of the existing solvent recovery unit.

Although the existing plant operated safely there have been proposals, however, to install ammonia detection apparatus within the protective booth and to use this to isolate electrical equipment if the atmospheric concentration exceeds some fraction of the L.E.L. of ammonia (if this is done it will be important to make provision for manually by-passing the solenoid valve in the water drenching line).

Finally, although a satisfactory sampling technique and method of analysis of samples was established this was time consuming and tedious. Connection of a mass spectrometer with a suitably designed, completely sealed, evaporation cell (with provision for heating to vaporise

all of the sample) to the extraction plant would allow samples to be withdrawn rapidly; instant analysis of samples would be possible.

Related Study

Since some uncertainty arose regarding the hydrodynamics and drop-sizes in the small R.D.C., related non-mass transfer studies could be performed in a geometrically-similar glass column using a binary system of similar physical properties. This would enable drop sizes and hold-ups to be measured under very similar hydrodynamic conditions (i.e. flowrates, phase ratios and rotor speeds). Such a column has recently been designed on the basis of this study, and commissioned (121). The system has a $\Delta\rho$ = 0.192 g/cc., μ_c = 1.817 cp., γ = 8.85 dyne/cm., operation with an M.I.B.K. - Water system ($\Delta\rho$ = 0.1791 g/cc., μ = 0.584 cp., γ = 9.35 dyne/cm., would give reasonably close results. Properties could be adjusted more closely by partitioning a solute between the phases (122).

Finally, use of the equipment is not restricted to liquid ammonia; other solvents such as Freon or, in theory, liquid sulphur dioxide could be recovered and recycled by the existing refrigeration cycle.

APPENDIX

Appendix 1A

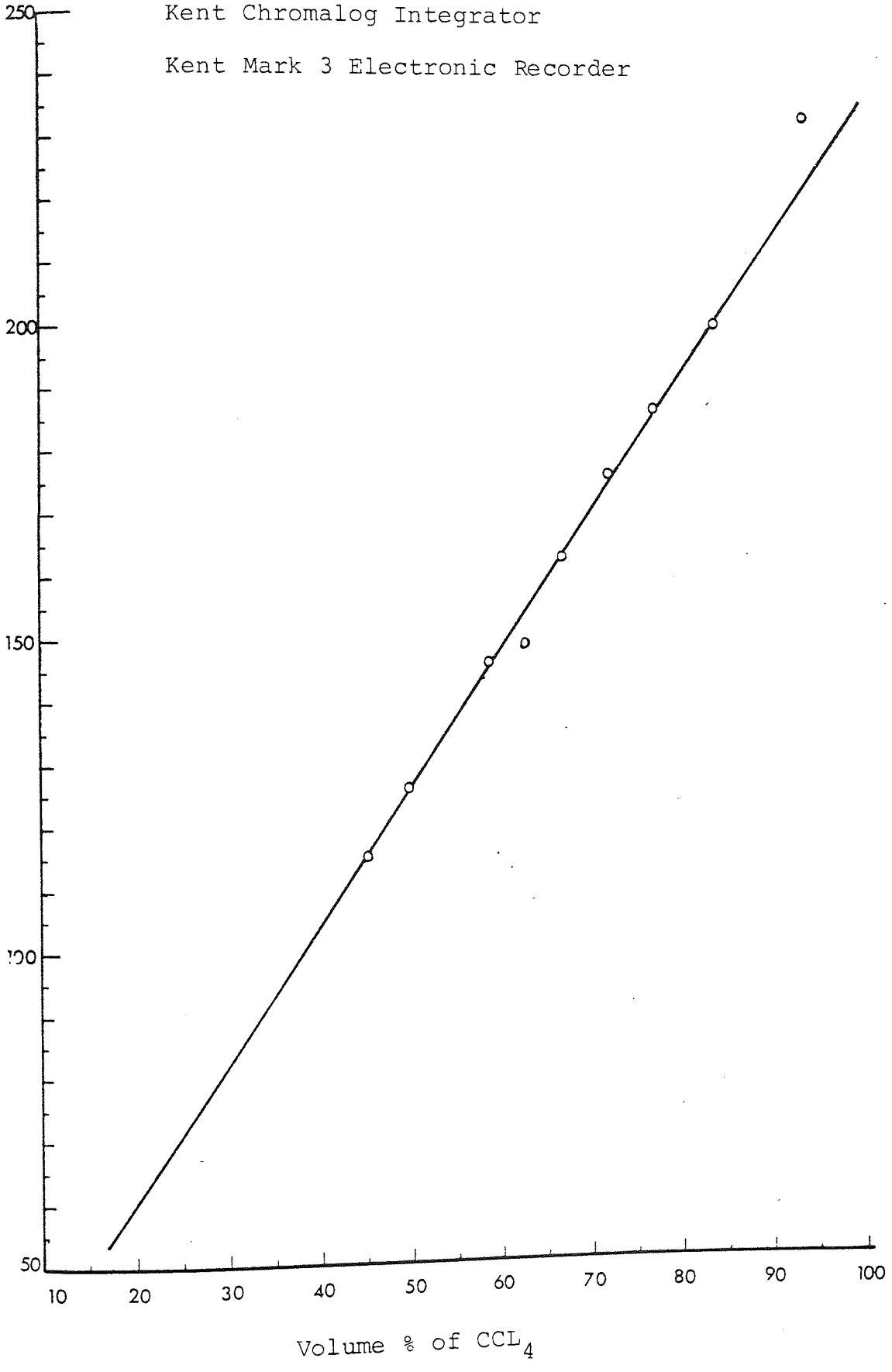
VOLUMETRIC COMPOSITION vs INTEGRATOR VALUES

SYSTEM: CCL_4 - Heptane - Cumene

Analysis of Equilibrium Studies, I

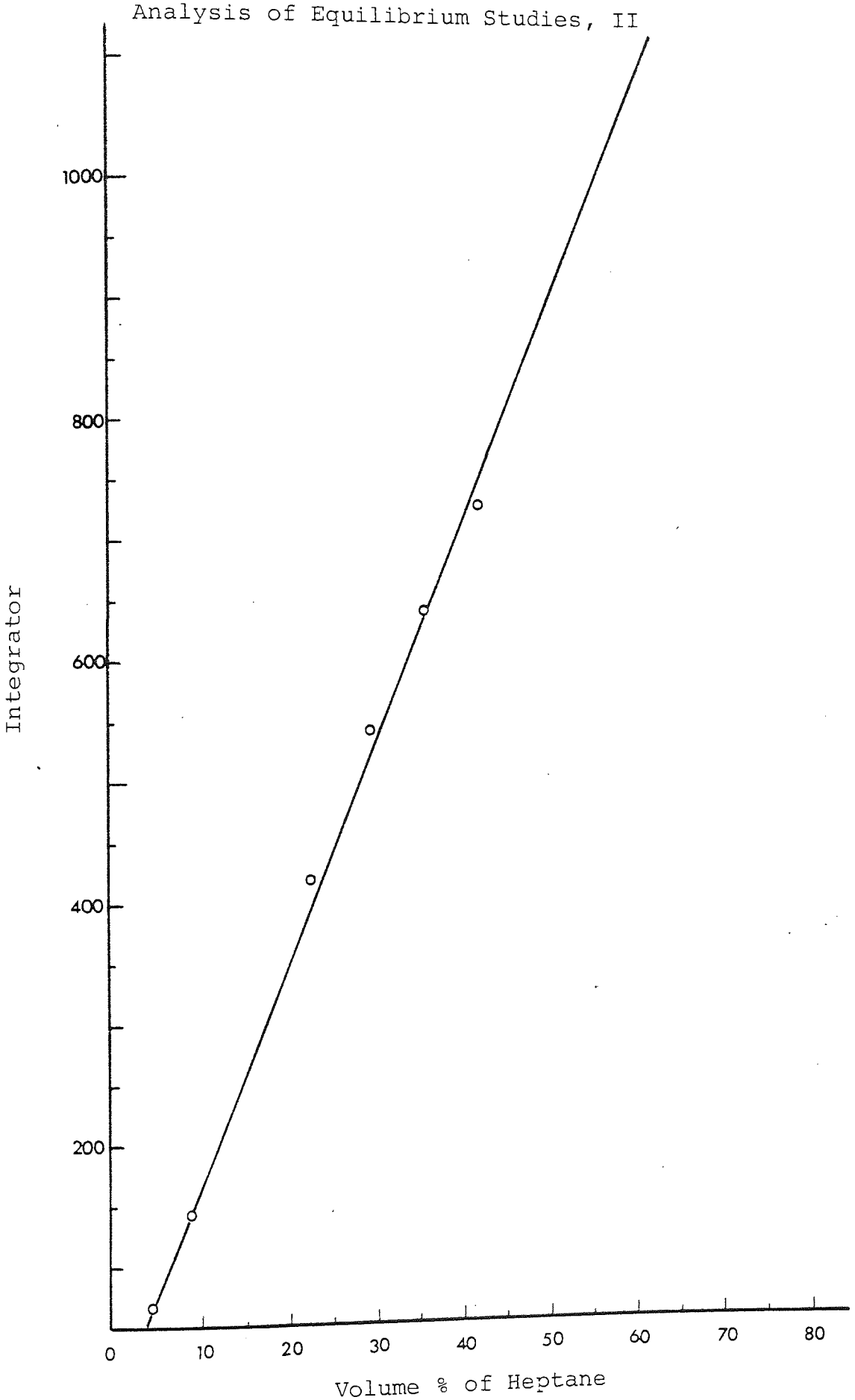
Kent Chromalog Integrator

Kent Mark 3 Electronic Recorder



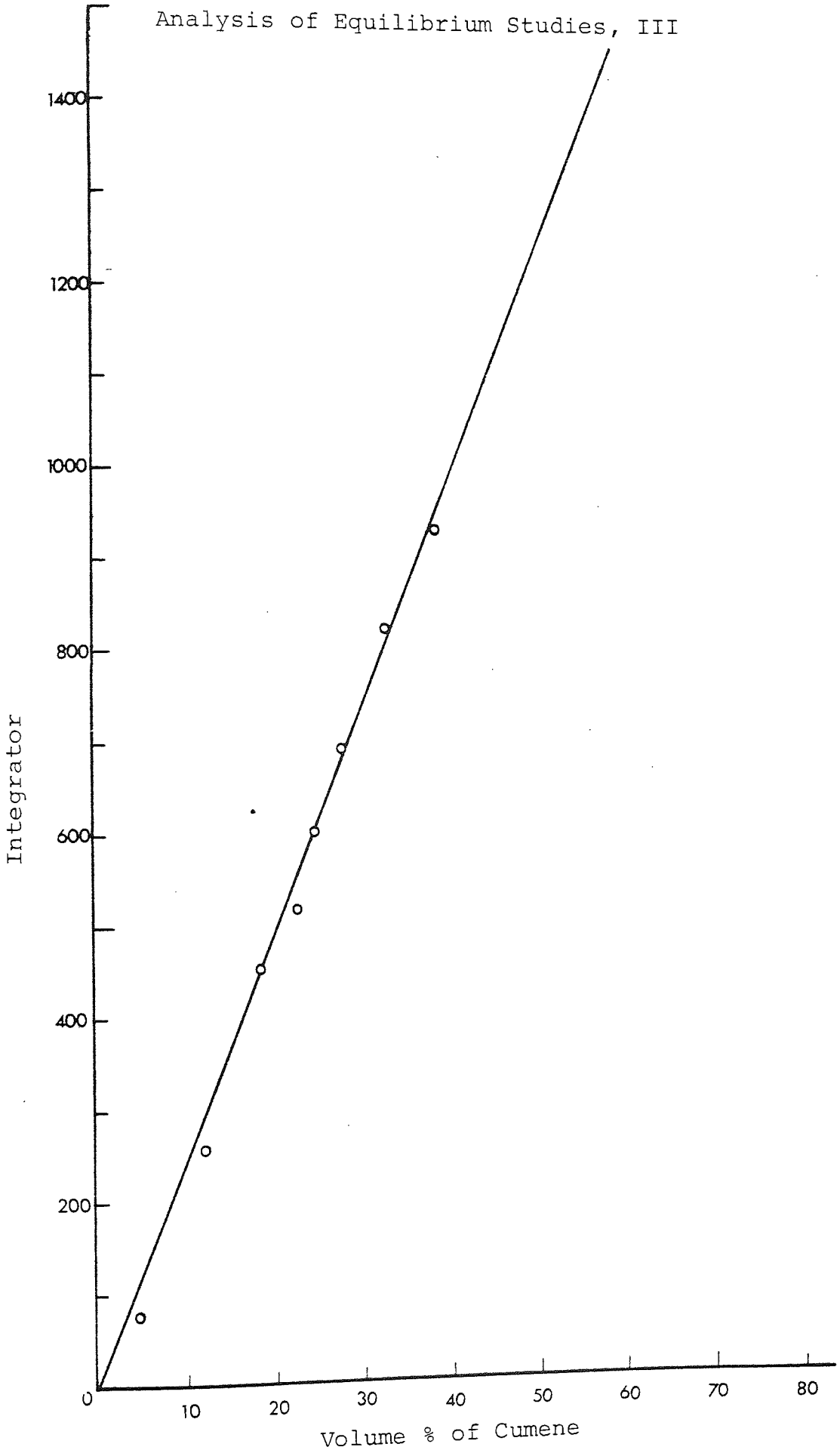
SYSTEM: CCL_4 - Heptane - Cumene

Analysis of Equilibrium Studies, II



SYSTEM: CCL_4 - Heptane - Cumene

Analysis of Equilibrium Studies, III



Appendix 1B

I Calculation of Equilibrium Data

Each experiment was carried out with a different feed composition. Experiments were designated 1S to 8S, and the samples identified by this reference followed by another number. The composition of feed in the bomb was first determined and hence the feed point positioned on the triangular diagram. The method of analysis of the products obtained is described in Section 5.3. A specimen calculation for 5S is given below, and the results of the other experiments are given in Appendix 1C.

Experiment 5S

Sample 5S1:

Determination of feed composition:

Hydrocarbons feed = 300. ml.

Volumetric composition of H/C.

Heptane = 45%

Cumene = 55%

Amount of NH_3 in the bomb:

Height of liquid measured by AVO meter after filling NH_3 = 69 mm.

Volume of liquid = Height x Area.

= 629.73 ml.

Volume of NH_3 = 629.73 - 300 = 329.73 ml.

Volumetric feed composition (i.e. point M5)

	Volume (ml.)	%
NH_3	329.73	52.36
Heptane	135.00	21.44
Cumene	165.00	26.20
Total	629.73	100.00

Sample 5S1

Hydrocarbons analysis by FID

	Integrator	% (vol)	Correction %	Volume (cc)
CCl_4	58	19	44.06	10.00
Heptane	199	11.38	26.38	5.99
Cumene	277	12.75	29.56	6.71
		43.13	100.00	22.70

Amount of NH_3 in the Sample

25cc solution titrated against 21.8 ml. 05 N. NaOH

Total solution = 100 ml N. H_2SO_4 i.e. 4.904 g. H_2SO_4

H_2SO_4 unreacted:

From:

$$H_2SO_4 + 2\ NaOH \longrightarrow Na_2SO_4 + 2\ H_2O$$

$21.8 \times 4 \times \frac{20}{1000}$ = 1.744 g. NaOH is used for titrating 100 ml. solution.

H_2SO_4 reacted with NaOH; $1.744 \times \frac{98}{80} = 2.1364$ g.

H_2SO_4 reacted with $NH_3 = 4.904 - 2.1364 = 2.7676$ g.

Amount of ammonia $= 2.7676 \times \frac{34}{98} = 0.9602$ g.

$$= \frac{0.9602}{0.611} = 1.5715 \text{ ml.}$$

	Volume (ml)	%
NH_3	1.57	11.00
Heptane	5.99	41.98
Cumene	6.71	47.02
Total	14.27	100.00

Similarly:

Sample 5S2

Hydrocarbons analysis by F.I.D

	Integrator	%(Vol.)	Corrected %	Volume (ml)
CCl_4	128	51.00	48.57	10.00
Heptane	480	25.75	24.52	5.05
Cumene	704	28.25	26.91	5.54
		105.00	100.00	20.59

Amount of NH_3 in the sample:

25cc solution titrated against 20.7 ml. 0.5 N. NaOH

H_2SO_4 total; 100 ml. N. i.e. 4904 g. H_2SO_4

H_2SO_4 unreacted = 2.0286 g.

H_2SO_4 reacted with NH_3 = 2.8754 g.

Amount of NH_3 = 0.9976 g. = 1.64 ml.

	Volume (ml)	%
NH_3	1.64	13.41
Heptane	5.05	41.29
Cumene	5.54	45.30
	12.23	100.00

Sample 5S3

Hydrocarbons analysis by FID

	Integrator	Vol. %	Corrected	Volume
CCl_4	120	47.33	45.04	10
Heptane	501	26.88	25.58	5.68
Cumene	777	30.87	28.38	6.52
Total		105.08	100.00	22.20

Amount of NH_3

25 cc. Solution titrated against 18.5 cc. 0.5 N. NaOH

Total solution 100 cc. N. H_2SO_4 i.e. 4.904 g. H_2SO_4

H_2SO_4 unreacted = 1.813 g.

H_2SO_4 reacted with NH_3 = 3.091 g.

Amount of NH_3 = 1.0723 g. = 1.7514 cc.

	Volume	%
NH_3	1.75	12.55
Heptane	5.68	40.71
Cumene	6.52	46.74
Total	13.95	100.00

Appendix 1C

	Integrator	Volume %	Corrected Volume %	Volume (ml.)
Bottom Layer : IS1				
CCl_4	82	29.00	40.99	10.00
Heptane	661	35.25	49.82	12.16
Cumene	111	6.5	9.19	2.24
Total		70.75	100.00	24.40
Ammonia				1.79
Bottom Layer : IS2				
CCl_4	82	37.25	41.10	10.00
Heptane	869	46.23	51.02	12.43
Cumene	127	7.15	7.88	1.92
Total		90.63	100.00	24.35
Ammonia				1.32
Bottom Layer : IS3				
CCl_4	95	36.50	41.19	10.00
Heptane	855	45.50	51.34	12.47
Cumene	115	6.63	7.47	1.81
Total		88.63	100.00	24.28
Ammonia				1.02
Top Layer : IS4				
CCl_4	221	93.30	90.10	10.00
Heptane	124	7.50	7.24	0.80
Cumene	23	2.75	2.66	0.29
Total		103.55	100.00	11.09
Ammonia				14.17
Top Layer : IS5				
CCl_4	229	97.00	94.75	10.00
Heptane	38	3.00	2.93	0.31
Cumene	19	2.38	2.32	0.24
Total		102.38	100.00	10.55
Ammonia				15.17
Bottom Layer : 2S1				
CCl_4	91	33.33	40.86	10.00
Heptane	695	37.00	45.35	11.10
Cumene	238	11.25	13.79	3.38
Total		81.58	100.00	24.48
Ammonia				1.09
Bottom Layer : 2S2				
CCl_4	85	31.33	40.06	10.00
Heptane	682	36.25	46.35	11.57
Cumene	223	10.63	13.59	3.39
Total		78.21	100.00	24.96
Ammonia				1.27

	Integrator	Volume %	Corrected Volume %	Volume (ml.)
Bottom Layer : 2S3				
CCl_4	89	32.75	40.06	10.00
Heptane	711	38.00	46.48	11.60
Cumene	232	11.00	13.46	3.36
Total		81.75	100.00	24.96
Ammonia				1.23
Top Layer : 2S4				
CCl_4	215	90.67	89.02	10.00
Heptane	113	6.85	6.73	0.75
Cumeme	36	4.33	4.25	0.48
Total		101.85	100.00	11.23
Ammonia				13.45
Bottom Layer : 3S1				
CCl_4	99	37.00	42.84	10.00
Heptane	610	32.37	37.48	8.75
Cumene	397	17.00	19.68	4.57
Total		86.37	100.00	23.32
Ammonia				2.13
Bottom Layer : 3S2				
CCl_4	64	21.88	39.95	10.00
Heptane	405	21.88	39.95	10.00
Cumene	232	11.00	20.10	5.03
Total		54.76	100.00	25.03
Ammonia				1.33
Bottom Layer : 3S3				
CCl_4	97	36.67	41.73	10.00
Heptane	628	33.38	37.98	9.10
Cumene	408	17.83	20.29	4.86
Total		87.88	100.00	23.96
Ammonia				1.19
Top Layer : 3S4				
CCl_4	182	75.33	89.36	10.00
Heptane	43	3.25	3.86	0.43
Cumene	86	5.63	6.68	0.75
Total		84.21	100.00	11.18
Ammonia				12.01
Top Layer : 3S5				
CCl_4	226	95.67	91.73	10.00
Heptane	47	3.50	3.36	0.37
Cumene	75	5.13	4.91	0.54
Total		104.30	100.00	10.91
Ammonia				12.60

	Integrator	Volume %	Corrected Volume %	Volume (ml.)
Bottom Layer : 4S1				
CCl_4	53	21.03	44.26	10.00
Heptane	268	15.00	31.55	7.13
Cumene	252	11.50	21.19	5.47
Total		47.53	100.00	22.60
Ammonia				1.36
Bottom Layer : 4S2				
CCl_4	95	36.16	44.08	10.00
Heptane	476	25.63	31.24	7.09
Cumene	488	20.25	24.68	5.60
Total		82.04	100.00	22.69
Ammonia				1.40
Top Layer : 4S3				
CCl_4	226	95.50	93.13	10.00
Heptane	21	2.05	2.00	0.21
Cumene	81	5.00	4.87	0.52
Total		102.55	100.00	10.73
Ammonia				12.25
Top Layer : 4S4				
CCl_4	217	91.33	90.80	10.00
Heptane	48	3.50	3.48	0.38
Cumene	92	5.75	5.72	0.63
Total		100.58	100.00	11.01
Ammonia				11.98
Bottom Layer : 5S1				
CCl_4	58	19.00	44.06	10.00
Heptane	199	11.38	26.38	5.99
Cumene	277	12.75	29.56	6.71
Total		43.13	100.00	22.70
Ammonia				1.57
Bottom Layer : 5S2				
CCl_4	128	51.00	48.57	10.00
Heptane	480	25.75	24.52	5.05
Cumene	704	28.25	26.91	5.54
Total		105.00	100.00	20.59
Ammonia				1.64
Bottom Layer : 5S3				
CCl_4	120	47.33	45.04	10.00
Heptane	501	26.88	25.58	5.68
Cumene	777	30.87	29.38	6.52
Total		105.08	100.00	22.20
Ammonia				1.75

	Integrator	Volume %	Corrected Volume %	Volume (ml.)
Bottom Layer : 5S4				
CCl_4	129	51.50	45.68	10.00
Heptane	532	28.50	25.28	5.53
Cumene	826	32.75	29.04	6.36
Total		112.75	100.00	21.89
Ammonia				1.77
Top Layer : 5S5				
CCl_4	246	104.50	85.57	10.00
Heptane	65	4.25	3.48	0.41
Cumene	296	13.38	10.95	1.28
Total		122.13	100.00	11.69
Ammonia				13.77
Top Layer : 5S6				
CCl_4	244	102.75	84.22	10.00
Heptane	73	3.75	3.07	0.37
Cumene	356	15.50	12.71	1.51
Total		122.20	100.00	11.88
Ammonia				13.72
Bottom Layer : 6S1				
CCl_4	101	38.50	44.57	10.00
Heptane	325	17.88	20.69	4.64
Cumene	751	30.00	34.74	7.79
Total		86.38	100.00	22.43
Ammonia				2.24
Bottom Layer : 6S2				
CCl_4	96	36.67	43.96	10.00
Heptane	302	16.75	20.08	4.57
Cumene	751	30.00	35.96	8.18
Total		83.42	100.00	22.75
Ammonia				2.28
Bottom Layer : 6S3				
CCl_4	99	37.67	44.23	10.00
Heptane	312	17.25	20.25	4.58
Cumene	757	30.25	35.52	8.03
Total		85.17	100.00	22.61
Ammonia				2.27
Top Layer : 6S4				
CCl_4	190	79.00	79.30	10.00
Heptane	66	4.38	4.39	0.55
Cumene	377	16.25	16.31	2.06
Total		99.63	100.00	12.61
Ammonia				12.80

	Integrator	Volume %	Corrected Volume %	Volume (ml.)
Top Layer : 6S5				
CCl_4	190	79.00	81.23	10.00
Heptane	46	3.50	3.60	0.44
Cumene	334	14.75	15.17	1.87
Total		97.25	100.00	12.31
Ammonia				13.14
Top Layer : 6S6				
CCl_4	190	79.00	80.41	10.00
Heptane	44	3.37	3.43	0.43
Cumene	365	15.88	16.16	2.01
Total		98.25	100.00	12.44
Ammonia				13.07
Bottom Layer : 7S1				
CCl_4	115	45.17	48.87	10.00
Heptane	232	13.25	14.34	2.93
Cumene	833	34.00	36.79	7.53
Total		92.42	100.00	20.46
Ammonia				2.34
Bottom Layer : 7S2				
CCl_4	103	39.67	45.51	10.00
Heptane	233	13.25	15.20	3.34
Cumene	862	34.25	39.29	8.63
Total		87.17	100.00	21.97
Ammonia				2.44
Bottom Layer : 7S3				
CCl_4	109	41.88	45.83	10.00
Heptane	244	13.75	15.05	3.28
Cumene	913	35.75	39.12	8.54
Total		91.38	100.00	21.82
Ammonia				2.43
Bottom Layer : 7S4				
CCl_4	95	36.33	44.47	10.00
Heptane	218	12.37	15.14	3.41
Cumene	833	33.00	40.39	9.08
Total		81.70	100.00	22.49
Ammonia				2.44
Top Layer : 7S5				
CCl_4	145	58.67	78.78	10.00
Heptane	25	2.60	3.49	0.44
Cumene	296	13.20	17.73	2.25
Total		74.67	100.00	12.69
Ammonia				12.20

	Integrator	Volume %	Corrected Volume %	Volume (ml.)
Top Layer : 7S6				
CCl_4	194	81.00	79.71	10.00
Heptane	44	3.38	3.32	0.42
Cumene	401	17.25	16.97	2.13
Total		101.63	100.00	12.55
Ammonia				12.13
Top Layer : 7S7				
CCl_4	197	82.33	79.58	10.00
Heptane	41	3.25	3.14	0.39
Cumene	421	17.88	17.28	2.17
Total		103.46	100.00	12.56
Ammonia				12.10
Bottom Layer : 8S1				
CCl_4	103	39.83	45.29	10.00
Heptane	103	6.38	7.25	1.60
Cumene	1070	41.75	48.46	10.48
Total		87.96	100.00	22.08
Ammonia				3.91
Bottom Layer : 8S2				
CCl_4	115	45.17	48.16	10.00
Heptane	105	6.50	6.93	1.44
Cumene	1085	42.13	44.91	9.33
Total		93.80	100.00	20.77
Ammonia				3.92
Bottom Layer : 8S3				
CCl_4	109	43.33	47.26	10.00
Heptane	101	6.25	6.97	1.48
Cumene	1050	41.00	45.77	9.68
Total		89.58	100.00	21.16
Ammonia				3.85
Bottom Layer : 8S4				
CCl_4	109	42.33	46.82	10.00
Heptane	99	6.20	6.86	1.47
Cumene	1077	41.88	46.32	9.89
Total		90.41	100.00	21.36
Ammonia				3.78
Top Layer : 8S5				
CCl_4	178	73.67	75.12	10.00
Heptane	13	2.00	2.04	0.27
Cumene	548	22.40	22.84	3.04
Total		98.07	100.00	13.31
Ammonia				11.89

	Integrator	Volume %	Corrected Volume %	Volume (ml.)
	Top Layer : 8S6			
CCl_4	174	71.67	73.53	10.00
Heptane	13	2.20	2.26	0.30
Cumene	562	23.60	24.21	3.30
Total		97.47	100.00	13.60
Ammonia				11.71

Appendix 1D

S	Feed	1S1	1S2	1S3	1S4	1S5
Ammonia	48.15	11.06	8.43	6.67	92.86	96.50
Heptane	45.63	75.11	79.32	81.50	5.24	1.97
Cumene	6.22	13.83	12.25	11.83	1.90	1.53
Total Vol. (ml.)	578.63	16.19	15.67	15.30	15.26	15.72

2S	Feed	2S1	2S2	2S3	2S4
Ammonia	36.96	7.00	7.83	7.62	91.62
Heptane	48.80	71.29	71.29	71.65	5.11
Cumene	14.24	21.71	20.88	20.75	3.27
Total Vol. (ml.)	460.00	15.57	16.23	16.19	14.68

3S	Feed	3S1	3S2	3S3	3S4	3S5
Ammonia	44.00	13.79	8.13	7.86	91.07	93.26
Heptane	36.96	56.63	61.13	60.06	3.27	2.74
Cumene	19.04	29.58	30.74	32.08	5.66	4.00
Total Vol. (ml.)	535.73	15.45	16.36	15.15	13.19	13.51

4S	Feed	4S1	4S2	4S3	4S4
Ammonia	42.15	9.74	9.94	94.37	92.22
Heptane	31.78	51.08	50.32	1.62	2.93
Cumene	26.07	39.18	39.74	4.01	4.85
Total Vol. (ml.)	456.33	13.96	14.09	12.98	12.99

5S	Feed	5S1	5S2	5S3	5S4	5S5	5S6
Ammonia	52.36	11.00	13.41	12.55	12.96	89.07	87.95
Heptane	21.44	41.98	41.29	40.71	40.48	2.65	2.37
Cumene	26.20	47.02	45.30	46.74	46.56	8.28	9.68
Total Vol. (ml.)	629.73	14.27	12.23	13.95	13.66	15.46	15.60

6S	Feed	6S1	6S2	6S3	6S4	6S5	6S6
Ammonia	48.68	15.27	15.17	15.26	83.06	85.05	84.27
Heptane	17.96	31.63	30.41	30.77	3.57	2.85	2.77
Cumene	33.36	53.10	54.42	53.97	13.37	12.10	12.96
Total Vol. (ml.)	584.56	14.67	15.03	14.88	15.41	15.45	15.51

7S	Feed	7S1	7S2	7S3	7S4	7S5	7S6	7S7
Ammonia	51.69	18.28	16.93	17.05	16.34	81.93	82.63	82.53
Heptane	12.08	22.89	23.18	23.02	22.84	2.95	2.86	2.67
Cumene	36.23	58.83	59.89	59.93	60.82	15.12	14.51	14.80
Total Vol. (ml.)	621.06	12.80	14.41	14.25	14.93	14.89	14.68	14.66

8S	Feed	8S1	8S2	8S3	8S4	8S5	8S6
Ammonia	36.13	24.45	26.68	25.65	24.97	78.22	76.49
Heptane	7.30	10.01	9.80	9.86	9.71	1.78	1.96
Cumene	56.57	65.54	63.52	64.49	65.32	20.00	21.55
Total Vol. (ml.)	657.57	15.99	14.69	15.01	15.14	15.20	15.31

Appendix 2

HYDROCARBON SELECTION FOR EXTRACTION WITH AMMONIA

Hydrocarbon	m.p. (°C)	b.p. (°C)	mol. wt. (g/cm^3)	ρ (g/cm^3)	Purity %	Solubility in NH_3 at 20°C (wt.%)	£/litre	TLV-TWA pp.m	TLV-TWA mg/m
n-Decane	-30.0	174.0	142.25	0.73	98	0.55	**25.28	-	-
n-Undecane	-26.0	196.0	156.31	0.74	99	<0.5	***64.70	-	-
n-Tetradecane	5.86	253.7	198.40	0.763	99	2.3	***45.10	-	-
Trimethylpentane	-107.4	99.24	114.2	0.692	99.5	1.7	**4.74	-	-
Methylcyclohexane	-126.59	100.9	98.19	0.769	99	4.6	*2.20	400	1600
n-Heptane	-91.0	98.0	100.21	0.684	99.5	2.3	*1.87	400	1600
1, 2, 4 Trimethylbenzene	-44.0	168.0	120.2	0.889	99	20.0	**19.62	25	120
Isopropylbenzene (cumene)	-96.0	152.0	120.2	0.864	99	45.0	**3.30	50	245
1, 2, 4, 5 Tetramethylbenzene	-80.8	190.0	134.2	0.838	98	15.0	***38.30	-	-
n-Butylbenzene	-85.0	169.0	134.5	0.871	98	17.0	***125.6	-	-
Toluene	-95.0	110.6	92.15	0.866	99	Completely miscible	*1.05	100	375

TLV-TWA = Threshold Limit Value, Time Weighted Average concentration for a normal 8 hr. work day or 40 hr. work week without adverse effect (113).

Costs are for maximum volumes available for convenient use, and minimum acceptable quality for this work.

* 25 litre can
** .500 ml. bottle
***100 ml. bottle

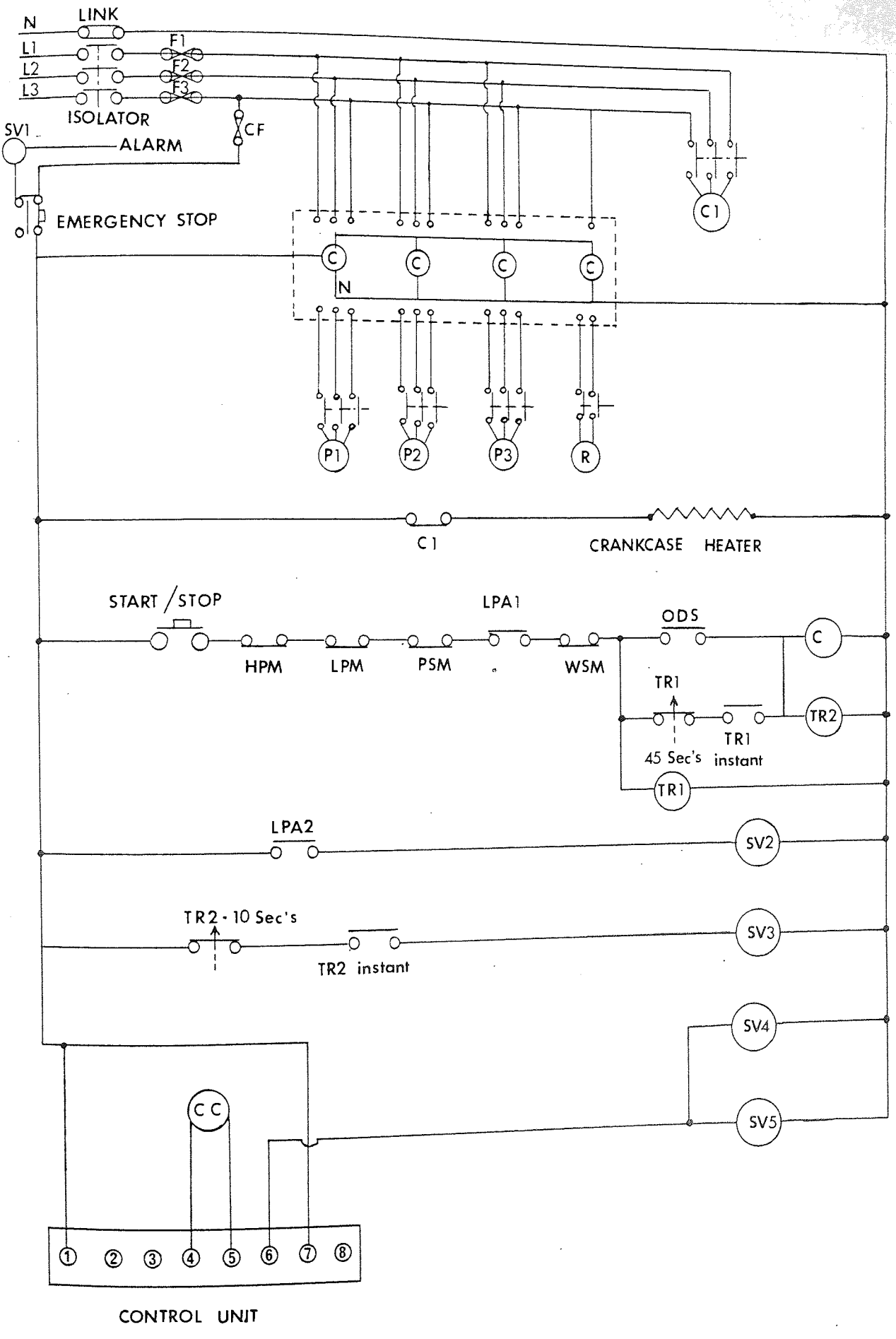
Appendix 3

ROTAMETERS SPECIFICATION

	R1	R2	R3
Size	1/2"	1/4"	3/8"
Model Number	7603L3270A2	7603L3270A1	7603L3271A2
Tube Number	FP-½-17-G-10/55	FP-¼-25-G-5/81	FP-3/8-20-G-5/81
Float Number	½-GSVT-44	¼-Dia-Ball	3/8-Dia-Ball
Float Material	Stainless Steel	Tantalum	Stainless Steel
Fitting Material	Stainless Steel	Stainless Steel	Stainless Steel
'O' Ring Material	Buna -N-	Nitrile	Nitrile
Flowrate Range	3-0.25 l/min.	1-0.08 l/min.	1.5-0.15 l/min.
Design Pressure	21 bar	35 bar	35 bar
Maximum Operating Pressure	10.3 bar	10.3 bar	10.3 bar

Appendix 4

ELECTRIC CONTROL CIRCUIT



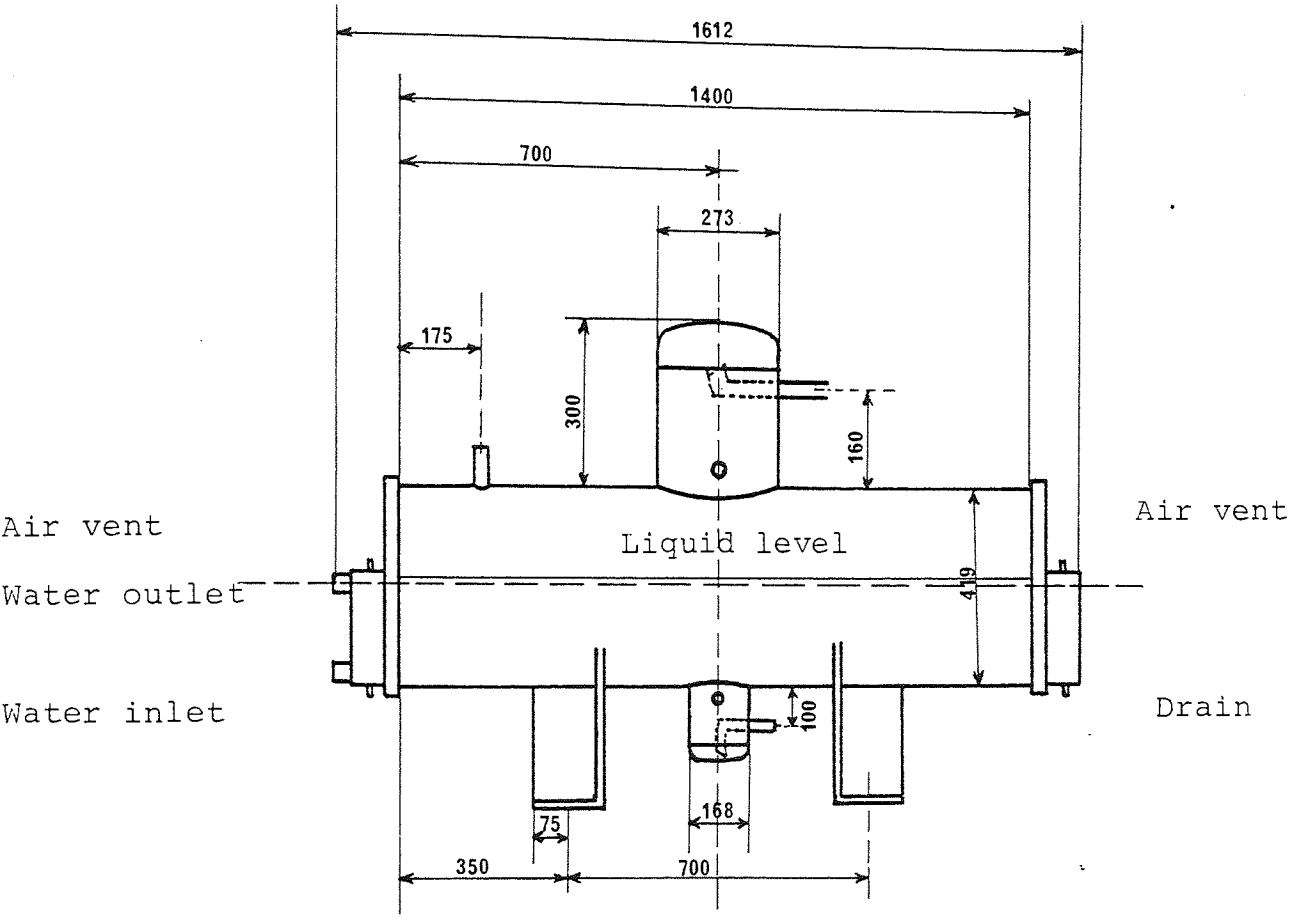
Key to Figure A4

F1, 2, 3	Main fuses
CF	Control fuse
HPM	High pressure cutout manual reset
LPM	Low pressure cutout automatic reset
LPA1, 2	Low pressure cutout automatic reset
SV1	Water spray solenoid
SV2, SV3	Cylinder head solenoids
SV4 & SV5	Flow control solenoids
ODS	Oil differential switch
CC	Control coil
PSM	Pressure switch manual reset
WSM	Evaporator, condenser water switch manual reset
P1, P2, P3	Pumps for ammonia, feed, reflux/feed respectively
TR1, 2	Time relay

Appendix 5A

EVAPORATOR DIMENSIONS AND SPECIFICATION

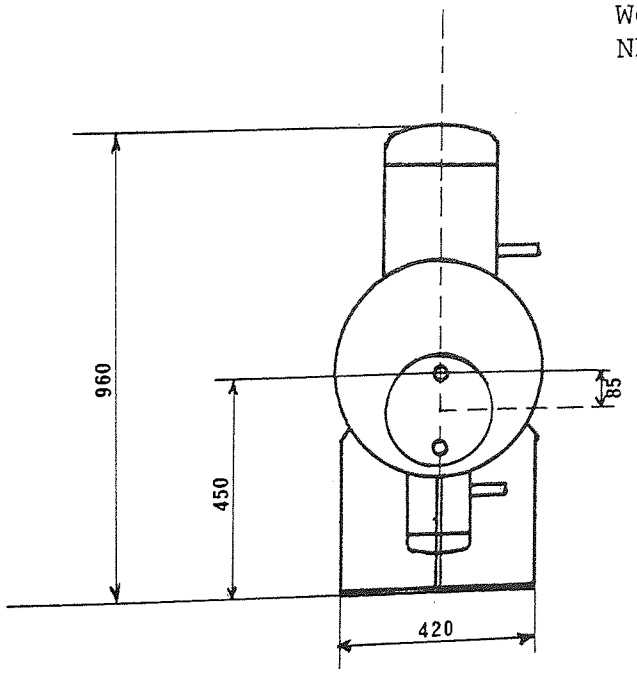
(All dimensions are in mm.'s)



a) Plan view

Data

Capacity = 16700 Kcal/h.
NH_3 (vol.) = 158 dm^3
Water (vol.) = 14 dm^3
Surface area = 3.68 m^2
Weight = 330 kg.
NH_3 inlet temp. = -9.5°C



b) Cross sectional view

APPENDIX 5B

COMPRESSOR SPECIFICATION

Crankcase and cylinder housing. This is an integral iron casting. Easy access to the interior of the compressor for inspection, cleaning, or adjustment of motionwork can be gained by removing the back-end cover, or a single side cover provided for this purpose. All sizes are fitted with an oil level sight glass and drain plug.

Crankshaft. The two-throw type crankshaft is manufactured from a high grade spheroidal graphite iron, accurately machined and with fine ground finish bearing surfaces. Each crankpin mounts two, three or four big-end bearings. The shaft is dynamically balanced to minimise vibration. It is carried on two wrapped bimetallic bushes within the crankcase. When necessary this type of bearing can easily be replaced. Steel backed white metal crankshaft thrust washers are fitted to each end of the crankcase. These are also easily renewable.

Crankshaft Gland Seal. The crankshaft is gas sealed at the gland end by a flexible mechanical seal, which is continuously lubricated and cooled by oil from the pressure feed system while the compressor is running.

Cylinder Liners. The liners are of high tensile cast iron with a fine ground external and honed internal finish.

Connecting Rods. The connecting rods are die-cast in aluminium alloy. There are no separate small and big end bearings, the alloy itself provides the bearing surfaces. The big end cap is so joined to the main body of the rod to give a bias to the connecting bolts to the left or right, thus simplifying assembly and maintenance.

Cylinder Head Cooling. Compressors operating on ammonia refrigerant are fitted with cylinder heads and covers suitable for water cooling.

Pistons. The pistons are made in an aluminium alloy. They are fitted with two compression rings. The lower ring is stepped to provide efficient gas sealing and good oil control.

Valves. Suction and delivery valves are of the reed type which effectively contribute to the quiet operation of the compressor.

Gas Strainer. The four cylinder machine is provided with an external strainer and the six and eight cylinder with a gas strainer conveniently housed in the front cover of the machine. These strainers are made from double crimped woven stainless steel wire cloth and can be removed for cleaning without difficulty. A felt filter is provided for fitting inside the strainer during the compressor running-in period, to trap scale and other impurities scoured from the system by the refrigerant.

Delivery Manifold. The delivery manifold is a common header integral with the crankcase into which gas from the several cylinders is discharged. The manifold is so designed to present the minimum heat exchange surface between suction and delivery gas passages. This feature assumes importance when the machine is used as an ammonia compressor.

Lubrication. Oil under pressure is supplied to all bearings and crankshaft seal by means of a vane pump driven directly from the end of the crankshaft. Oil in the sump is drawn into the pump section through a fine mesh strainer and delivered to the bearings. A crankcase oil level sight glass is fitted. Oil contained in the refrigerant returning to the compressor suction is separated from the gas in a low velocity suction chamber,which is common with the crankcase for the four cylinder and located in the front cover for the six and eight cylinder compressors. In the two larger sizes the separated oil drains back into the sump, and a froth breaker fitted between the crankcase and the suction chamber allows the crankcase to vent without loss of oil. The compressor is protected against oil failure by a differential oil switch, which causes the compressor to stop should the pressure fall below a pre-determined minimum.

Unloading Equipment. (Delivery gas operated) Manual automatic unloading equipment built into the cylinder heads can be provided to give light load start and capacity reduction, or, light load start only. The standard arrangement for the four cylinder machine is to unload one bank of two cylinders which provides 50% unloaded start with 50% capacity reduction. For the six cylinder machine four cylinders are unloaded in two pairs which provides $66\frac{2}{3}\%$ unloaded start with $33\frac{1}{3}\%$ and $66\frac{2}{3}\%$ capacity reduction and for the eight cylinder machine, six cylinders are unloaded in three pairs, which provides 75% unloaded start with 25% 50% and 75% capacity reduction.

Rotation. Designed to run in either direction.
The normal rotation of the compressor is clockwise when looking on the driven end. If required, anti-clockwise machines can be built to order.

Accessories
Differential oil pressure switch.
Main delivery and suction stop valves with companion flanges.
Set of tools. Operating and maintenance instructions.
Suction and delivery refrigerant pressure gauges with pressure/temperature dial scales. Oil pressure gauges.

Crankcase Oil Heater. An immersion type crankcase oil heater is normally required for compressors operating on refrigerants R.12 or R.22 and for ammonia compressors working on a high saturated suction gas temperature and a low ambient temperature. This type of heater is energised when the compressor stops and de-energised when it starts. The heating of the oil when the machine is stopped prevents the formation of liquid refrigerant and frothing of the oil on starting.

Appendix 5C

CONDENSER SPECIFICATION

Type = Shell and Tube (36-18/5'0")
Duty = 80,000 Btu/h. (23.45 kJ/s.)
Shell size = 32.4 cm. o.d.
Tubes size = 32.cm. o.d. 11 s.w.g.
Tube length = 152 cm.
Number of tubes = 18
Number of passes = 2
Surface area = 5.47 m^2
Dry weight = 363 kg.
Working weight = 417 kg.

	Main pressure shell	Water box shells
Design pressure	21.09 kg/cm^2	5.27 kg/cm^2
Hydraulic test pressure	35.15 kg/cm^2	10.55 kg/cm^2
Air test pressure	21.09 kg/cm^2	-

Temperature rise of cooling water between 4.4-8.8°C.

Difference between condensation temperature and cooling water inlet temperature not less than 5.5°C.

Water velocity 2.44-0.91 m/sec.

Appendix 5D1

SOLVENT RECOVERY UNIT TESTING PRIOR TO CHARGING

On no account is the refrigerating compressor to be used as an air compressor either for testing or for any other purpose

When the plant has been completely erected it should be subjected to a pressure test, in order to see that all joints, fittings, etc., have been correctly made and are sound.

Clean out the crankcase and fill to the correct level with refrigerating oil.

All valves throughout the system, with the exception of charging, drain and purge valves, should be wide open.

Dry nitrogen in cylinders is supplied for pressure testing. Connect the flask of nitrogen to the charging valve by means of the charging pipe. Open all valves throughout the system, including the hand regulator and the charging valve. The valve on the nitrogen flask can then be slightly opened and the nitrogen allowed to enter the system slowly until the pressure throughout is raised to 200 lb. sq. in. (14 kg. per sq. cm.). If it is necessary at any time to shut off the supply of nitrogen this should be done by means of the valve on the flask, and not by means of the charging valve. If the charging valve should be shut and the flask valve left open the full pressure of the nitrogen (about 2,000 lb. sq. in.) could be applied to the charging pipe, which would be dangerous.

All joints, including glands and welds, should be thoroughly tested for leaks by means of a soap and water solution. All drain, purge and charging valves should be opened to see if they are clear, and tight after closing.

When this has been satisfactorily carried out, the nitrogen should be blown out of the circuit from the most convenient point on the evaporator, such as a drain valve, and from the most convenient point nearest to the regulator on the condenser side of this valve.

Special instructions for low pressure controls

Low pressure controls are made to be sensitive at comparatively low pressures and can be badly damaged and rendered inaccurate if exposed to high pressures. It is most important therefore that, when carrying out pressure tests on completion of erection, all low pressure controls are either disconnected, or isolated by their stop valves, from the system for the whole duration of the high pressure tests.

Evacuating and dehydrating the plant

After the pressure test has been carried out the whole system must be completely evacuated before charging in the refrigerant. To be effective this evacuation must be continued until an absolute pressure of no more than 2 mms. absolute is obtained. In order to do this a special vacuum pump and gauges are necessary. This procedure not only removes all the air in the system but, at the same time, causes any moisture to be evaporated and removed.

The principle underlying this is the fact that water like refrigerant has an exact pressure temperature relationship, e.g. at ordinary atmospheric pressure water boils at 212°F. whereas at an absolute pressure of 0·1 lb./sq. inch (29·80" Hg. vacuum) it boils at 35°F. Hence by reducing the pressure sufficiently any moisture in the system can be made to boil, or evaporate and the resultant vapour is drawn off by the vacuum pump, leaving the system quite dry.

In order to evacuate the plant it is necessary to have all valves throughout the system wide open, as for testing. If there is no hand regulator, it will also be necessary to connect both high and low sides of the system to the vacuum pump as an effective vacuum cannot be obtained by trying to draw the vapour through the compressor valves. A careful check must be made to see that no part of the system is isolated by electro-magnetic valves, back pressure valve or other obstruction.

Evacuation should continue until a pressure no higher than 2 mms. mercury absolute has been attained. A joint should be slackened off, or valve in the system should then be opened at a point as far from the vacuum pump as possible, and the pressure in the system allowed to come up to atmospheric.

The joint should then be tightened up, or the valve shut, and the system again evacuated to 2 mms. mercury or better. The pump should then be isolated by shutting off the stop valves where it is connected to the system. The pump can then be stopped.

N.B.—The vacuum pump should never be switched off before isolating it otherwise oil from the pump will be drawn into the system and the vacuum lost.

The time to reach the desired degree of vacuum will depend on the amount of moisture, if any, in the sytem and the size of the plant. Drying is much more rapid in a warm room than in a cold one. If the ambient temperature is below about 45°F. it is advisable to continue pumping until an absolute pressure of 1 mms. Hg. is obtained.

Failure to obtain the necessary vacuum may be due to: —

(a) Leak in system or in connecting pipe line between vacuum gauge and plant.

(b) Defective vacuum pump or gauge.

(c) Ambient temperature too low.

(d) Parts of the system blanked off.

(e) Pressure of absorbed refrigerant in the crankcase oil.

When evacuation is complete the plant should be allowed to stand under the vacuum for several hours. If at the end of that time no rise in pressure has occurred the plant is ready for charging.

IMPORTANT.—When charging into an evacuated system, allow vapour only to enter the system very slowly until the pressure built up is well above atmospheric. If refrigerant is allowed to enter too quickly it will cause a very rapid cooling of the components and may cause damage.

If a vacuum pump is not available an alternative method of testing R12 and R22 plants is to pressure test with the refrigerant to be used in the plant.

This method should only be used in emergency as moisture will not be removed without the use of a vacuum pump.

The air is removed from the plant by a systematic purging, section by section, whereby the air is pushed out by the refrigerant as it is admitted.

When putting the refrigerant into the plant, it is essential to remove all the air present and, in the case where additional refrigerant is needed, to prevent the entrance of air through the charging pipe. It is preferable to waste a little refrigerant to ensure that all the air has been removed.

CAUTION—CO_2 (Carbon Dioxide) must not be used for pressure testing this plant.

APPENDIX 5D2

SOLVENT RECOVERY UNIT CHARGING

The approximate weight of refrigerant required to charge the plant will be found at the beginning of this manual.

Each flask, after it is connected to the charging valve on the liquid line by means of the charging pipe, should be carefully weighed so that a record can be made of the quantity of refrigerant inserted.

The flask should be held in an upright position, so that the vacuum in the system is broken by charging in the refrigerant in vapour form and not as a liquid.

Purge the charging pipe of air by opening the flask valve before completely tightening the connection on the charging valve. As vapour begins to escape, tighten the connection.

Open the flask valve and the charging valve fully and allow refrigerant vapour to pass into the system. This process should be carried on until the pressure in the system is equal to the pressure in the flask, when the flow will cease. The pressure obtainable is dependent upon the type of refrigerant and the ambient temperature.

When the pressure has equalized and has ceased to rise, the flask should be inverted so that charging in the next stage will continue by the insertion of refrigerant in the liquid state.

With the condenser water or air flowing, and the cooled medium being circulated through the evaporator, the compressor should be started, and operated at minimum capacity to prevent it being stopped by the low pressure control switch or safety cut-out. The liquid stop valve at the outlet from the condenser must be 'throttled in' as necessary to reduce the pressure in the liquid line, thereby inducing the refrigerant to flow into the system from the charging flask.

CAUTION.—Under no circumstances should the low temperature cut-out be disconnected or put out of action in any way during this process.

Continue charging the plant in this manner, loading the compressor in relation to the available evaporator load, until approximately 75 per cent. of the estimated total charge has been inserted. The balance should be charged in whilst the plant is running under full load conditions, as this will influence the total charge required. To do this the remaining charge must be admitted intermittently alternating with the plant operating normally with the liquid line stop valve fully open, and the charging valve closed. During these periods observation of the operating conditions will show the correctness of the charge.

The system is fully charged when the evaporator or evaporators are operating at their desired capacities simultaneously, assuming that there is adequate compressor capacity. An evaporator will operate at full capacity only when it is supplied with sufficient liquid refrigerant to contact all of its heat transfer surface. Any portion of the surface not 'wetted,' i.e. not in contact with the refrigerant in its liquid state, but in contact with the refrigerant in its dry or superheated vapour state, is practically ineffective.

If the system is equipped with a liquid receiver which is in circuit whilst the plant is operating normally, the receiver sight-glass will show a level when the plant is operating at design conditions, showing that high pressure vapour is unable to enter the liquid line.

If the system is equipped with a liquid line sight-glass, this will not show bubbles in the liquid when the plant is fully charged.

NOTE.—The liquid stop valve at the receiver or condenser outlet must be fully open when observing the liquid line sight-glass. If this is restricted it will cause a reduction in pressure so that liquid will 'flash off' producing bubbles in the sight-glass.

If the system is fitted with a liquid line thermometer, this should read approximately 5° F. below the condensation temperature as shown on the condenser gauge, showing that the liquid refrigerant is being slightly subcooled.

Overcharge

1. Systems with H.P. Float Regulators—

The effect of an overcharge would be to overfill the evaporator which could result in

iquid refrigerant being carried over into the compressor, with consequent damage to the valves and motion work.

2. Systems with L.P. Float or Thermostatic Regulators—

The effect of an overcharge would be to overfill the condenser which would result in the condensing pressure rising to an excessive level with a consequential rise in the power consumption of the compressor motor. If the condenser is overfilled to a marked degree, this would result in a sudden and rapid rise in the condensing pressure which could result in the compressor safety disc bursting.

Appendix 5E

COMPRESSOR OPERATION

(Starting, running, stopping)

To start the compressor

The following procedure is recommended as the method to follow when starting the compressor: —

1. See that the level of the oil is one-third to one-half way up the sight-glass in the crankcase.

   In a newly commissioned plant, it will be necessary from time to time to replenish the level of oil in the crankcase, until the oil content of the refrigerating system as a whole has become stabilised.

   The design of the circuit on which the compressor is operating may be such that it traps a quantity of oil preventing it from returning with the suction gas. In such cases the trapped oil is removed from the circuit after passing through an oil rectification system, and either returned automatically to the crankcase, or drained manually from the plant. In the latter instance the oil lost from the crankcase must be replenished periodically.

   If it is continually found necessary to add oil to a plant from which none has been drained, it is advisable to seek the advice of H T I.

2. See that all pressure gauge valves are open. Make sure that the isolating valves on either side of the oil filter are open.

3. In the case of some manually controlled compressors it is possible, although not essential, to flood the bearings before starting. (See Section 5).

4. Check that all valves in the condenser water circulating system are open.

5. Start condenser water flowing and check for adequate flow through the condenser and through cylinder head jackets when fitted.

6. Open compressor suction and delivery stop valves. (The compressor must never be started with the delivery stop valve closed or partially closed).

7. See that all other stop valves throughout the circuit are fully open except the following: —

   Air purge valves.

   Drain valves.

   Main liquid stop valve at condenser refrigerant outlet.

   Pre-set regulators on multi-circuit systems.

   Hand regulator(s).

   (If a pump is fitted for refrigerant circulation the hand regulator(s) should be cracked open immediately before starting the liquid pump).

   Charging valve.

   Oil return stop valve from delivery oil separator or rectifier.

   Liquid stop valve to crankcase oil cooler (when fitted).

   Valves marked .....
   .....
   .....
   .....
   .....
   on the gas diagram, Drawing No. ..... at the end of this manual.

8. Start circulation through the evaporator of the water, brine or other fluid to be cooled. In direct expansion air cooling applications start the fan.

9. Start liquid pump (when fitted).

10. Start the compressor. Unless the liquid level in the evaporator has been allowed to become unduly high, no trouble should be experienced with liquid passing over to the compressor.

11. Open the main liquid stop valve wide.

12. Open oil return valve from oil rectifier or delivery oil separator. If a delivery oil separator is fitted, the oil return valve from it to the crankcase should be opened only very slowly and only after the separator is warm throughout its length.

    It has been found that even then some liquid refrigerant may still remain in the separator and if the oil return valve is opened too quickly this will enter the crankcase and cause the oil to be pumped out.

13. When the temperature of the external oil filter on the compressor reaches about 120°F. (this is warm to the touch) the liquid stop valve for the crankcase oil cooler can be opened. (This applies only to compressors with oil coolers and only to manually controlled plants and the initial start up of automatic plants).

NOTE.—When starting the compressor with the evaporator warm, it may be necessary, in order to reduce the load on the motor or to keep the condenser gauge within reasonable limits, to partially close the suction stop valve. This must be carried out very slowly and cautiously as a sudden reduction in the suction pressure will result in the oil being pumped out of the crankcase. The suction stop valve should never be closed in so far that the suction gauge falls to a lower level than would be experienced with the plant operating at design conditions. As the evaporator pressure falls, the suction stop valve should be re-opened.

With compressors with manually-operated capacity reduction gear, all cylinders so equipped should be unloaded as an alternative to closing in the suction stop valve.

Regulation

The evaporator will only operate at full capacity when it is supplied with sufficient liquid refrigerant to contact all of its heat transfer surface. Any portion of the surface not 'wetted,' e.g. not in contact with the refrigerant in its liquid state, but in contact with the refrigerant in its dry or superheated vapour state, will be practically ineffective.

The rate at which the refrigerant is admitted to the evaporator is controlled by the regulator or expansion valve. This must be adjusted, either manually or automatically, to meter a quantity of liquid refrigerant into the evaporator which is such that the vapour entering the compressor suction is superheated to a level which will ensure that liquid droplets are not entrained. The degree of suction superheat can be ascertained by observing the difference between the suction gas temperature and the saturation temperature of the refrigerant at the pressure as shown on the suction gauge.

The suction superheat will depend to a large extent upon the design of the evaporator. On ammonia plants utilizing a flooded type of evaporator the superheat will be approximately 5°F. to 10°F., or 15°F. to 20°F., on plants utilizing direct expansion evaporators with thermostatic expansion valves. On R12 and R22 plants, the suction superheat should be approximately 15°F. to 20°F., or approximately 30°F. to 40°F., if a suction line to liquid line heat exchanger is incorporated in the system.

If the degree of suction superheat is allowed to become too high, this will in turn raise the discharge gas temperature. Conversely, if the suction gas temperature falls, the discharge temperature will follow. If liquid droplets are allowed to enter the compressor, the discharge temperature will fall considerably.

A table giving the approximate discharge gas temperature of a correctly regulated plant under different operating conditions is included later in this section. It should be noted that discharge gas temperatures are not critical to within 5°F. to 10°F. of the figures given in the table.

1. Manual regulation

When the plant is to be manually regulated, the regulator(s) should be opened very slowly as soon as the plant has been started. It must be adjusted to give the correct operating conditions, closing it slightly if there is evidence of excess liquid in the evaporator, i.e. the suction gas temperature not sufficiently superheated; or opening it slightly if the suction gas temperature becomes too high, due to a shortage of liquid in the evaporator.

One-tenth of a turn is usually quite sufficient adjustment to make at one time. It must be remembered that if the evaporator is large, a considerable time may elapse before the full effect of a change in regulation is obtained or observed.

If the plant has been started with the evaporator at a high temperature, it will be necessary to gradually close the regulator as the temperature falls.

Steady operating conditions and easy regulation can only be obtained when the plant is correctly charged.

2. Automatic regulation

The total refrigerant charge in an automatic plant is more critical than in one operating on

hand control. This is especially the case when an H.P. float regulator is fitted. The function of this type of regulator is to drain the condenser of liquid refrigerant as it is formed. The condenser cannot therefore be used as an accumulator for surplus charge as would be the case when working with an L.P float or thermostatic regulator.

Excessive charge in a system with an H.P. float regulator will result in the evaporator being overcharged, with the result that liquid may enter the compressor.

If liquid refrigerant enters the compressor, or the compressor pumps out the oil from the crankcase, the safety heads will lift. If this should occur, the compressor will be heard to 'knock.' Under no circumstances whatever should the compressor be allowed to run for any length of time with the safety heads lifting, as the incompressibility of the oil or liquid refrigerant will result in the valves being broken. Should the safety heads lift for more than a few minutes, steps must be taken to rectify the cause.

An evaporator designed to work at low temperatures will hold a greater charge of refrigerant at the low temperature than at a temperature 20° or 30° higher such as occurs when first cooling down the system. The reason for this is that at the higher evaporating temperature, the compressor will do very much more work, thus increasing considerably the rate of boiling in the evaporator. Consequently, there is a much larger proportion of gas to liquid present in the evaporator, therefore less weight of refrigerant can be accommodated.

For this reason, it is advisable to use the hand regulator when first cooling down a system fitted with an H.P. float regulator or an H.P. pilot-operated regulator. Alternatively, close in the suction stop valve slightly or reduce the output of the compressor.

In some installations, particularly marine, a plant may be required to work under either high or low temperature evaporator gauge conditions with an H.P. float regulator or an H.P. pilot-operated regulator. In this instance a liquid receiver or reservoir is provided into which some of the charge must be transferred when the plant is working at the higher evaporator gauge.

When an L.P. float or thermostatic regulator is fitted in the system the effect of an overcharge will be to increase the condenser gauge temperature in relation to the cooling water temperature. An undercharge would lower the condenser gauge and increase the temperature of the liquid leaving the condenser.

With an L.P. float regulator great care must be taken in starting with a warm evaporator in order to avoid liquid entering the compressor suction. If manually-operated capacity reduction gear is fitted this should be in operation, on all cylinders so fitted, when starting, Alternatively, the suction stop valve should be used to restrict the flow of vapour into the compressor (see Note after paragraphs on starting procedure) immediately it has been started.

Discharge gas temperature

It has already been stated that the discharge gas temperature depends, among other things, on evaporator and condenser gauge temperature readings, and on the state of the gas charge.

Faulty valves may also cause the discharge gas temperature to be higher than normal. This is due to the fact that some gas leaks back past the faulty or broken valve and is re-compressed.

Discharge gas temperature in excess of 280°—300°F. should be avoided.

During running

With both automatically or manually controlled plants, it is important that during running, a routine procedure should be carried out to ascertain that the plant is functioning correctly. The most important points are listed below: —

1. The level of oil in the crankcase must be from one-third to half way up the oil level sight-glass in the crankcase when the compressor is running.
2. Regular and accurate logging of temperatures, pressures, etc., must be carried out. It is only by so doing that the performance of the plant can be accurately assessed and early warning obtained of any deviation from normal running. A specimen log sheet is included later in this section which sets out the minimum readings which it is necessary to record for this purpose. In many cases the number of essential readings may well be considerably more.
3. Suction and delivery gauge readings should be checked against the temperature of the cooled medium leaving the evaporator and the temperature of the condenser water respectively. Discharge gas temperatures should also be checked.

Liquid receiver or reservoir

Some plants are supplied with a liquid receiver or reservoir and it should be noted that if the regulator is an H.P. float or an H.P. pilot-operated regulator, the receiver is not in circuit when the plant is operating normally. The receiver or reservoir is used

as a storage vessel to hold the charge during overhaul or emergency periods, or to hold part of the charge if the plant is required to operate at a higher evaporating temperature than that for which the total charge has been adjusted. (See ' Automatic regulation ' earlier).

If an L.P. float regulator or a thermostatic regulator is fitted the receiver will normally be in circuit.

Shell and tube and multipass evaporators

In most plants fitted with this type of evaporator the fluid to be cooled passes through the tubes, consequently its temperature must always be kept substantially above its freezing point. In water-cooling plants, for example, the water temperature must not be allowed to fall below 38°F. Failure to observe this precaution will cause the fluid to freeze in the tubes with the inevitable result of damage to the evaporator and the loss of the whole gas charge.

A low temperature or low pressure cut-out, or both, are normally fitted to water-cooling plants as safeguards against possible freezing in the evaporator.

To stop the compressor

The following procedure for stopping the compressor is recommended: —

1. Shut main liquid stop valve, also liquid stop valve for the crankcase oil cooler (when fitted).
2. Shut oil return valve from delivery separator or oil rectifier and any other valves which connect the crankcase to the main circuit.
3. Switch off compressor motor and, as compressor comes to rest, close suction stop valve.
4. Shut off condenser water and circulation through cylinder head jackets (if fitted).
5. Stop circulation of medium being cooled.
6. Stop liquid pump (when fitted).

NOTE.—With a hand-regulated plant the regulator should never be used as a stop valve as this may damage the cone. Normally it is not necessary to interfere with the regulator when stopping the plant provided the liquid stop valve has been closed.

If the above procedure is adopted it will be found that re-starting becomes very much easier as there will be the correct amount of refrigerant in the evaporator and the danger of pumping liquid will be considerably reduced. Items (1) and (2) are particularly important in this respect. Some plants are provided with solenoid valves in certain of the pipelines in which case it is unnecessary also to close the manually-operated valves.

If the plant is to be shut down for a long period, say four hours or more, the compressor delivery stop valve should be closed.

When a delivery oil separator is fitted, the valve on the condenser side of the separator should be closed. This will prevent condensation in the separator whilst the plant is shut down.

Great care must be taken to see that all the appropriate valves are opened before re-starting.

Prolonged shut down

When a plant is shut down for a prolonged period it is important, in order to prevent leakage from the compressor gland seal, that the faces of the seal should be kept well lubricated. This can be achieved by running the compressor for a short time once or twice a week.

Automatic plants

For normal automatic working, manual operations should not be necessary. Where pumps or other auxiliaries are not required to run when the machine is idle, they are electrically interlocked with the main motor. If it is necessary for certain valves to be closed or opened they would be electrically or pressure operated so that they, too, were entirely automatic.

All that is necessary therefore with an automatic plant is to make regular inspections to ensure that pressures and temperatures in various parts of the system are normal and that an adequate level of oil is maintained in the crankcase.

Evaporators fitted with suction gas/liquid heat exchangers

When this type of unit is incorporated in the plant, the purpose of the heat exchanger is to ensure that only dry gas reaches the compressor suction.

In order to achieve this it is essential that there should be a temperature difference of 40°F. between the temperatures of evaporation and condensation.

Under conditions where the condensing temperature is low and the temperature of the brine, water or other medium in the evaporator is high, e.g. 60°F. and 35°F. respectively, the necessary temperature difference will not be achieved. In such cases the condenser water flow should be restricted in order to raise the condensing temperature to about 80°F.

In automatically controlled plants this adjustment would usually be carried out by the use of a pressure-operated water valve or similar device.

Running in compressor

In the early life of a new plant the refrigerant tends to have a scouring effect and in spite of the utmost care during manufacture and erection there is always the possibility of scale, etc., being released from the surface of the metal and ultimately finding its way into the crankcase.

In consequence of this it is most important that certain safeguards should be observed to protect the compressor during, approximately, the first 200 hours running.

Lubricating oil

In those plants fitted with an oil separator, oil which passes over into the separator is returned to the crankcase by way of the automatic oil return.

If the separator is of the M.P.S. type, a strainer will be incorporated in the oil return pipe. During the first 12 hours running of the compressor, a felt filter should be fitted in the strainer to remove very small particles of extraneous material that may be present in the oil. After this initial period the filter should be removed (i.e. at the same time as the suction strainer felt filter is changed, see later) and not replaced unless its condition indicates excessive contamination of the oil.

At the end of 200 hours the compressor and separator should have the oil drained from them, be thoroughly cleaned internally, and refilled with new oil.

To do this pump out the crankcase, as described in Section 4, isolating the separator by closing the stop valve on the condenser side, and carefully purging away the refrigerant vapour.

The compressor side or end covers should next be removed, together with the separator float valve assembly, and then the crankcase and the lower part of the separator shell cleaned. Clean rag of a non-fluffy texture only should be used for cleaning.

Suction strainer

The majority of dirt, scale, grit and other extraneous materials from both the compressor and/or the plant with which it is associated, invariably returns to the suction of the compressor during the first few hours of running. It is, therefore, important that extra care be taken during the initial operation of a plant to ensure that the suction strainer is efficient.

In the case of most of the Veebloc range of compressors, a label will be found wired to the suction flange which reads as follows: —

IMPORTANT

This machine is fitted with a felt filter which MUST be removed after 12 hours running. A spare filter and instructions, which MUST be removed prior to compressor running, are in the strainer basket.

On *all* compressors fitted with this label, it is *essential* that the suction strainer cover is removed and the spare felt filter and instructions are extracted, leaving the fitted felt filter in position, before starting the compressor.

The compressor should then be run for approximately 12 hours after which the compressor should be pumped out and the original felt filter removed. The spare felt filter should then be fitted and the compressor run for a further 90 or 100 hours after which time the second filter should be removed. If the system is particularly dirty it may be necessary to either clean the second filter or fit an additional replacement before this period has been completed.

It is undesirable to keep the felt filter in the strainer basket longer than is necessary, i.e., after the majority of the dirt has been removed from the system, as the felt filters, even when clean, cause a greater pressure drop than that experienced through the normal suction strainer. The effect of this unnecessary pressure drop would be to lower the refrigerating capacity of the compressor.

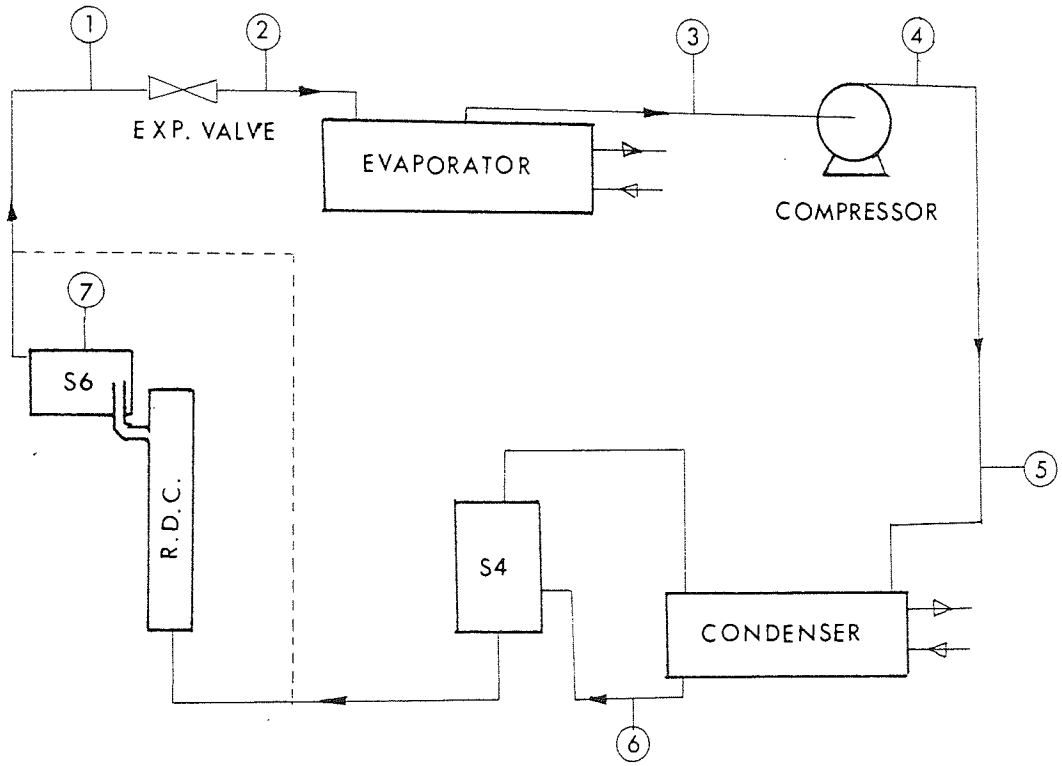
After the first 100 hours running with the felt filters incorporated in the suction strainer, the normal strainer basket should be adequate protection for the compressor. A watch should be kept however in case the strainer becomes partially choked which would reduce the compressor efficiency.

On compressors not fitted with felt filters, it is recommended that the suction strainer should be removed and cleaned after the first 12 hours running and then two or three times during the next 100 hours running.

Detailed instructions for pumping out the compressor and purging after opening up are given in Section 4 of the instruction book.

Appendix 6

SOLVENT RECOVERY UNIT, OPERATING CONDITION - EXPERIMENT 2



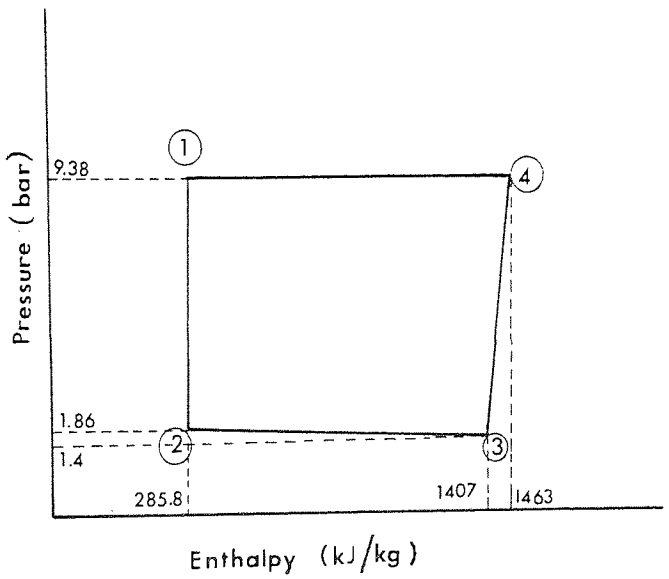
Temperature-Pressure Readings:

Point	Temperature C°	Pressure Bar	Pressure psi
1	21.8	9.38	136.
2	-6.	1.86	27.
3	12.5	1.4	20.3
4	66.	9.7	140.6
5	52.5	9.7	140.6
6	22.5	9.7	140.6
7	-	9.38	136.
Compressor oil	-	4.9	71.1

Water Temperatures

	Temperature ^{o}C
Inlet to condenser	12.5
Outlet to condenser	19.3
Inlet to evaporator	21.0
Outlet from evaporator	14.0

Solvent Recovery Unit as a refrigeration cycle



OPERABILITY STUDY

An operability study was carried out for the complete extraction plant. This study, covering each purpose of every line from each of the 7 vessels and the R.D.C. has been filed in the Department. An example of the procedure for just one line on one vessel is given below.

Vessel = S1. Storage of raffinate containing <10% ammonia in hydrocarbons
Temperature ambient, Pressure = Atmospheric - 7.6 bar.

Line = Raffinate inlet to transfer heavy product of R.D.C. (Also, at the start of each run, to transfer hydrocarbons from top settler to be replaced with ammonia).

Property	Guide Word	Cause	Consequence/Action
FLOW	NO.	Pressure in S1 >7.6 bar and same as in S6.	Interface level in S6 rises. Crack open V1 to vent S1 to obtain PI5<PI6.
		V42 blocked.	Check that V42 is blocked by cracking open V59 via SP1, if it is stop operation.
	LESS	V53, or V52 leaking (Pressure in S1>E1).	Raffinate flows into E1, slow increase of level in S1 (V42 open). Stop operation, change diaphragm of V53.
		V44 leaking.	Smell of ammonia. Stop operation, change diaphragm of V44.
		V42 is insufficiently open.	Interface level in S6 rises, slow increase of level in S1. Control raffinate flow to maintain interface level in S6 by adjusting V42.
	AS WELL AS	V52,V53 leaking (Pressure in S1<E1)	Extract flows into S1 via V52 or V53, rapid increase of level in S1, NH_3 content of raffinate higher than expected, valves and the pipe line feel cold, interface between phases might appear in level gauge S1. Stop operation and change diaphragms of V52 and V53.

Property	Guide Word	Cause	Consequence/Action
		Similar densities of heavy and light phases in R.D.C.	Ammonia flow into S1 with raffinate. Check from equilibrium data if twin density condition likely.
		V42 too wide open, (Pressure in S1<S6)	Flow of ammonia into S1 with raffinate, fall in interface level in S6, rapid level increase in S1. Adjust V42 to maintain interface level.
	MORE	V42 too much open.	Fall in interface level in S6. Adjust V42 to maintain interface level.
TEMPERATURE	LOW	Flashing of NH_3 through a leak.	Pipe lines and valves and joints frosted or feel cold.
	HIGH	None (no external heating).	
CONCENTRATION OF NH_3	LOW	Leakage from a joint or valve. Flashing of ammonia.	Raffinate contains more ammonia than expected Feel pipe lines and joints to find cold spots indicating ammonia leak to atmosphere.
	HIGH >20%	Same reasons as in property: flow, guide word = as well as	Same as property = flow, guide word: as well as

Safety warning

1. The electrical power used in this equipment is at a voltage high enough to endanger life.

2. Before carrying out maintenance or repair procedures, persons concerned must ensure that the equipment is isolated from the electrical supply and tests made to verify that isolation is complete. Whenever possible, precautions must be taken to prevent the circuit being inadvertently energised.

3. When the supply cannot be disconnected, functional testing, maintenance and repair of the electrical units is to be undertaken only by persons who are fully aware of the risk involved and who have taken adequate precautions to avoid direct contact with dangerous voltages.

4. Personnel must not start the compressor until they have taken steps to verify the following:—

   (a) Guards on couplings, belt drives and fans are in position, and other personnel are not in positions that are hazardous when the plant is in operation.

   (b) That the compressor discharge stop valve is fully open.

5. Personnel stopping a plant must ensure that they do not shut pipeline stop valves in such a manner as to trap cold liquid refrigerant between valves.

6. The plant is charged with Ammonia which is dangerous and has inherent material and physiological hazards. A limited range of ammonia air mixtures (16–27% ammonia by volume) can be ignited by flame and an explosion may result. Ammonia must not be allowed to come into contact with iodine, bromine, chlorine, hypochlorites or with mercury; there is an explosion hazard in each case.

7. Ammonia is not a cumulative poison, but because of its high affinity to water the immediate effects of exposure are as follows:—

   VAPOUR. Low concentrations may cause only irritation and discomfort; high concentrations can destroy body tissue. The action is more pronounced on moist tissues; eyes, breathing passages, and moist areas of the skin may be burned by high concentrations.

   LIQUID. This form can cause severe burning of the skin and eyes. In the case of eyes, even small amounts are harmful. The full effect of ammonia on the eyes may not be apparent for 8–10 days. but, ultimately, blindness may result.

8. Maintenance procedures must not be carried out unless adequate ventilation has been provided to avoid risk of explosion and physiological harm. Naked flame must not be permitted in the area. The pungency of ammonia will usually warn personnel against remaining in locations where dangerously high concentrations of vapour exists. Personnel must not be permitted to work without wearing a respirator, even for short periods, in a concentration which causes any discomfort to the eyes or affects the breathing.

Do not rely on an isolation valve when a line connecting with ammonia is broken, always use a blank flange as well. Rubber gloves and goggles must be worn when pipelines which have contained ammonia are broken. Gas masks suitable for protection against ammonia must be immediately available, preferably worn at the ready. All vessels and pipelines should be thoroughly purged of ammonia before starting operations likely to produce sparks or flame (e.g. welding). In addition precautions should be taken to prevent a dangerous build up of ammonia vapour during these operations.

Exits and gangways of buildings and engine rooms where ammonia is used or stored, must be kept clear and unobstructed to ensure that they can be rapidly vacated in the event of a serious escape of ammonia. If a leak occurs, open all doors and windows leading to the open air to accelerate ventiliation; If it is a leak of liquid, swill with large quantities of water whenever possible.

Gas masks, fitted with a cannister suitable for use with ammonia must be kept available for emergencies, and personnel must be trained in their use. For rescue work, in high concentrations of ammonia, air masks (transparent, rubber type) rubber boots and gloves are essential. Gas masks are effective only for relatively short periods and in low concentrations of gas only.

All locations from which evacuation can only be carried out with difficulty must be designated 'gas mask areas'. All persons entering such areas, must be thoroughly trained in the use of gas masks, and carry one at the ready.

Supplementary refrigerant must be in approved containers, and the quantity held in the plant room limited (see BS. 4434 para 15.5). Cylinders and drums of refrigerant must be treated with care.

KEEP AWAY FROM HEAT

DO NOT DROP

ENSURE THAT BLANKED CONNECTIONS ARE TIGHT.

Notices advising all safety precautions to be taken, and of emergency first aid treatment, should be displayed in areas where ammonia is used or stored.

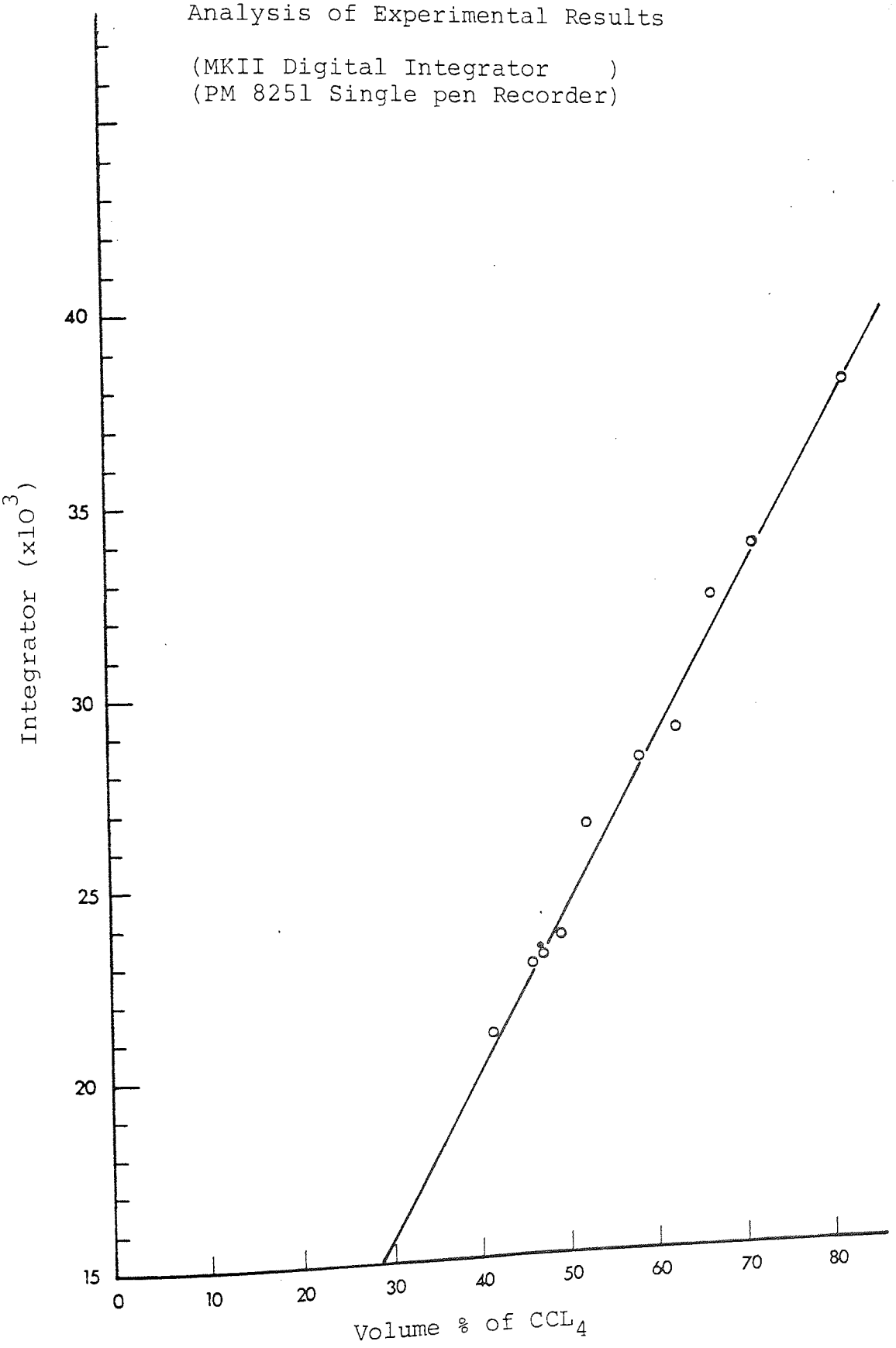
Appendix 9A

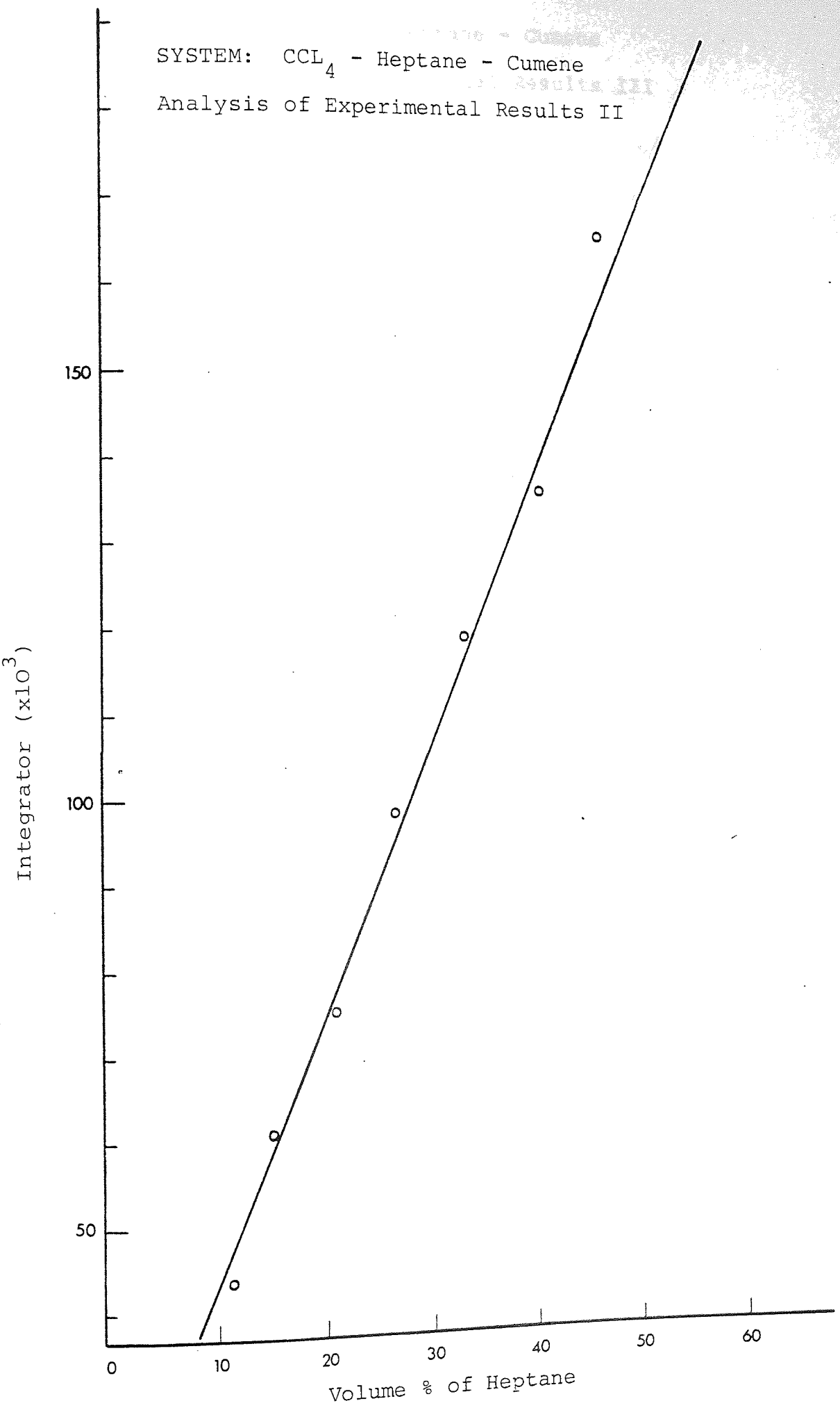
VOLUMETRIC COMPOSITION vs INTEGRATOR VALUES

SYSTEM: CCL_4 - Heptane - Cumene,

Analysis of Experimental Results

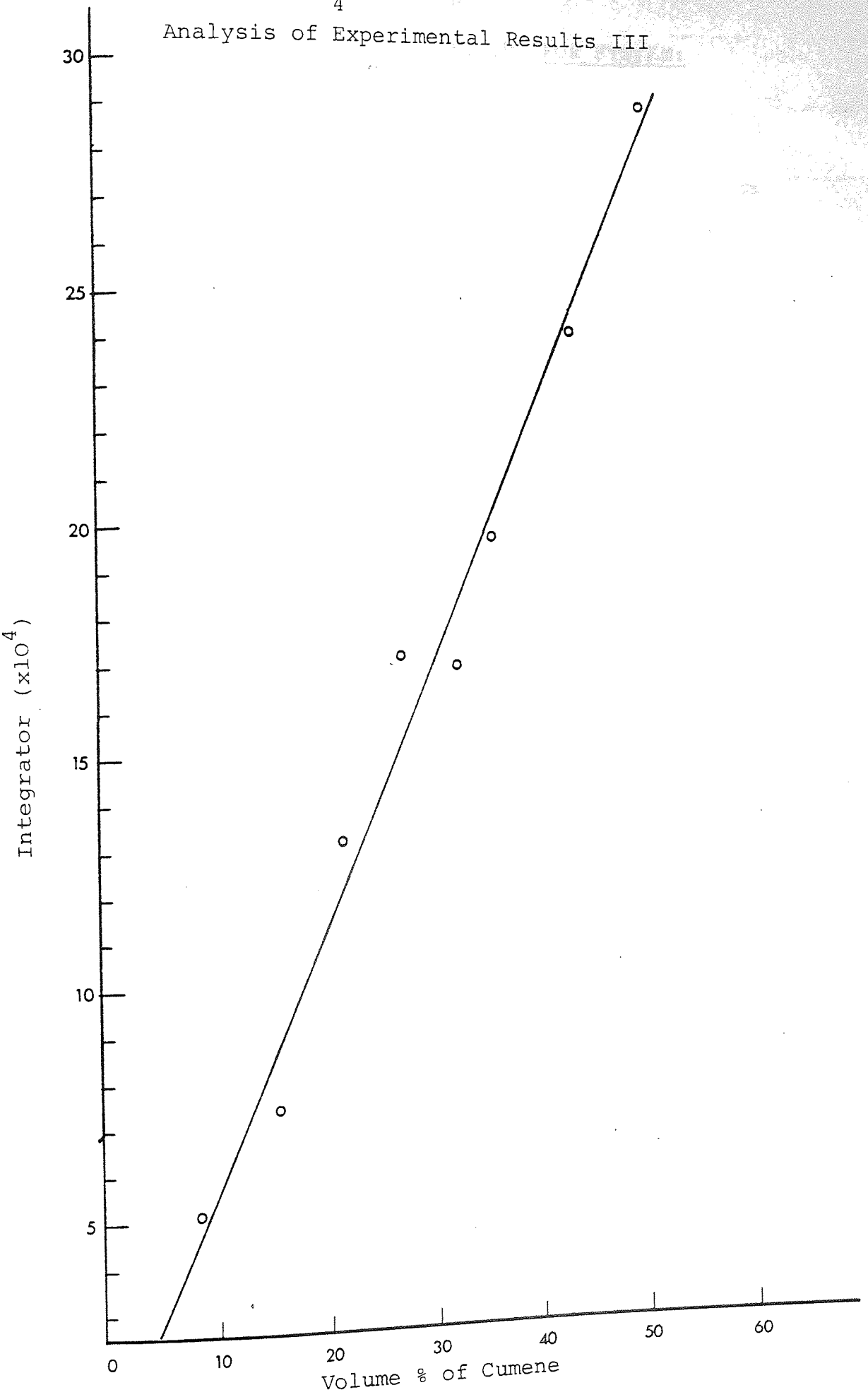
(MKII Digital Integrator)
(PM 8251 Single pen Recorder)




SYSTEM: CCL_4 - Heptane - Cumene
Analysis of Experimental Results II
Integrator ($x10^3$)
150
100
50
0
10
20
30
40
50
60
Volume % of Heptane

SYSTEM: CCL_4 - Heptane - Cumene

Analysis of Experimental Results III



Appendix 9B

HYDROCARBONS ANALYSIS BY F.I.D. FOR SYSTEM:

n-HEPTANE-CUMENE-AMMONIA

Experiment 1

Rotor Speed = 300 rpm.

2 samples were drawn from feed, raffinate and extract sampling points designated as F1, F2, R1, R2, E1, E2, respectively.

	Integrator	Vol. %	Corrected Vol. %	Vol. (cc)
F1				
CCl_4 Heptane Cumene	22191 166228 55616	45.0 47.7 10.05	43.8 46.4 9.8	10.0 10.59 2.24
Total		102.75	100.00	22.84
F2				
CCl_4 Heptane Cumene	28937 161972 55269	60.5 47.0 10.0	51.49 40.0 8.51	10.0 7.77 1.65
Total		117.5	100.00	19.42
R1				
CCl_4 Heptane Cumene	26293 131559 101998	54.5 37.7 17.8	49.55 34.27 16.18	10.0 6.91 3.27
Total		110.0	100.00	20.18
R2				
CCl_4 Heptane Cumene	18720 194868 49000	37.5 57.8 7.5	36.48 56.22 7.30	10.0 15.30 2.11
Total		102.8	100.00	27.41
E1				
CCl_4 Heptane Cumene	38910 43609 49781	83.5 9.7 8.9	81.78 9.50 8.72	10.00 1.16 1.07
Total		102.1	100.00	12.23

	Integrator	Vol. %	Corrected Vol. %	Vol. (cc)
E2				
CCl_4	43105	89.75	87.14	10.00
Heptane	31008	6.24	6.07	0.70
Cumene	40026	7.00	6.79	0.78
Total		100.00	100.00	11.48

periment 2

tor Speed = 600 r.p.m.

	Integrator	Vol. %	Corrected Vol.%	Volume
CCl_4	24011	49.10	46.99	10.00
Heptane	155412	45.25	43.30	9.21
Cumene	58770	10.15	9.71	2.07
Total		104.50	100.00	21.28
2				
CCl_4	22520	46.00	45.12	10.00
Heptane	158501	45.80	44.92	9.95
Cumene	55488	10.15	9.96	2.21
Total		101.95	100.00	22.16
1				
CCl_4	34067	72.5	62.61	10.00
Heptane	88152	24.3	20.98	3.35
Cumene	107211	19.0	16.41	2.62
Total		115.8	100.00	15.97
2				
CCl_4	28366	59.00	56.32	10.00
Heptane	121790	34.25	32.70	5.81
Cumene	63305	11.50	10.98	1.95
Total		104.75	100.00	17.76
1				
CCl_4	43211	93.5	89.26	10.00
Heptane	28306	5.5	5.25	0.59
Cumene	31671	5.75	5.49	0.61
Total		10.475	100.00	11.20
E2				
CCl_4 Heptane Cumene	Sample lost (due to leaking valve)			
Total				

tor speed = 300 r.p.m.

	Integrator	Vol. %	Corrected Vol. %	Vol. (cc.)
1				
CCl_4	24251	49.6	45.5	10.0
eptane	132373	37.8	34.68	7.62
umene	122911	21.6	19.82	4.36
otal		109.0	100.00	21.98
2				
CCl_4	21306	43.1	44.43	10.0
eptane	121018	34.4	35.46	7.98
umene	111414	19.5	20.11	4.53
otal		97.0	100.00	22.51
1				
CCl_4	39111	84.25	83.62	10.00
eptane	41602	9.5	9.43	1.13
umene	39165	7.0	6.95	0.83
Total		100.75	100.00	11.96
R2				
CCl_4	38077	81.5	91.32	10.00
Heptane	27500	5.0	5.60	0.62
Cumene	15208	2.75	3.08	0.33
Total		89.25	100.00	10.95
E1				
CCl_4	38611	82.5	80.68	10.00
Heptane	42065	9.5	9.29	1.15
Cumene	29920	10.25	10.03	1.24
Total		102.25	100.00	12.39
E2				
CCl_4	45538	99.00	96.12	10.00
Heptane	17056	1.75	1.70	0.17
Cumene	11178	2.25	2.18	0.23
Total		103.00	100.00	10.40

Experiment 4

Rotor speed = 600 r.p.m.

	Integrator	Vol. %	Corrected Vol. %	Vol. (cc)
F1				
CCl_4	22774	46.4	44.79	10.00
Heptane	128798	36.5	35.23	7.87
Cumene	117894	20.7	19.98	4.46
Total		103.6	100.00	22.33
F2				
CCl_4	2610=	54.25	54.44	10.00
Heptane	106097	29.5	29.60	5.44
Cumene	89971	15.9	15.96	2.93
Total		99.65	100.00	18.37
R1				
CCl_4	39247	84.3	68.93	10.00
Heptane	114941	32.0	26.17	3.80
Cumene	33984	6.0	4.90	0.71
Total		122.3	100.00	14.51
R2				
CCl_4	28821	60.5	56.02	10.00
Heptane	108233	30.5	28.24	5.04
Cumene	97177	17.0	15.74	2.81
Total		108.0	100.00	17.85
E1				
CCl_4	44535	96.0	82.4	10.00
Heptane	50829	12.5	10.73	1.30
Cumene	44811	8.0	6.87	0.84
Total		116.5	100.00	12.14
E2				
CCl_4	45447	98.2	79.55	10.00
Heptane	61264	15.75	12.75	1.60
Cumene	50600	9.5	7.7	0.97
Total		123.45	100.00	12.57

xperiment 5

otor speed = 300 r.p.m.

	Integrator	Vol. %	Corrected Vol. %	Vol. (cc).
F1				
CCl_4	22772	46.5	40.26	10.00
Heptane	118911	33.0	28.57	7.10
Cumene	200397	36.0	31.17	7.74
Total		115.5	100.00	24.84
F2				
CCl_4	23188	47.5	43.78	10.00
Heptane	106190	29.5	27.19	6.21
Cumene	179869	31.5	29.03	6.63
Total		108.5	100.00	22.84
R1				
CCl_4	25235	53.5	51.57	10.00
Heptane	119474	33.5	32.29	6.26
Cumene	94124	16.75	16.14	3.13
Total		103.75	100.00	19.39
R2				
CCl_4	35996	79.4	77.93	10.00
Heptane	38310	8.5	9.15	1.17
Cumene	56052	12.0	12.92	1.66
Total		92.9	100.00	12.83
E1				
CCl_4	31602	67.0	74.44	10.00
Heptane	42819	9.5	10.55	1.42
Cumene	75003	3.5	15.00	2.01
Total		90.00	100.00	13.43
E2				
CCl_4 Heptane Cumene	Sample lost (due to leaking valve)			
Total				

AMMONIA ANALYSIS BY TITRATION FOR SYSTEM:

n-HEPTANE-CUMENE-AMMONIA

	Vol. D.5.N. Nc_1OH used to titrate 25cc. I.N.H_2SO_4	Total H_2SO_4 Sol. (cc.)	NH_3 amount (cc.)
F1	47.7	100	0.13
F2	48.4	100	0.09
R1	5.4	500	12.42
R2	37.4	500	3.53
E1	20.4	500	8.24
E2	17.9	500	8.94
F1	48.8	100	0.07
F2	48.6	100	0.08
R1	40.7	500	2.60
R2	30.5	500	5.44
E1	20.3	500	8.27
E2	-	-	-
F1	48.0	100	0.11
F2	47.9	100	0.12
R1	27.0	500	6.43
R2	29.9	500	5.62
E1	33.3	500	4.66
E2	41.2	500	2.45
F1	46.1	100	0.22
F2	47.3	100	0.15
R1	45.1	500	1.38
R2	6.8	500	12.03
E1	24.3	500	7.16
E2	4.9	500	12.55
F1	45.5	100	0.25
F2	46.8	100	0.18
R1	42.9	500	1.99
R2	15.0	500	9.75
E1	11.00	500	10.86
E2	-	-	-

n-HEPTANE-CUMENE-AMMONIA

			Vol. (cc)	Vol. %		Vol. (cc)	Vol. %
Heptane	EX1	F1	10.59	81.71	F2	7.77	81.79
Cumene			2.24	17.29		1.65	17.37
Ammonia			0.13	1.00		0.09	0.94
Total			12.96	100.00		9.50	100.00
Heptane		R1	6.91	30.57	R2	15.50	73.06
Cumene			3.27	14.47		2.11	10.08
Ammonia			12.42	54.96		3.53	16.86
Total			22.60	100.00		20.94	100.00
Heptane		E1	1.16	11.08	E2	0.70	6.72
Cumene			1.07	10.22		0.78	7.49
Ammonia			8.24	78.70		8.94	85.79
Total			10.47	100.00		10.42	100.00
Heptane	EX2	F1	9.21	81.15	F2	9.95	81.29
Cumene			2.07	18.24		2.21	18.06
Ammonia			0.07	0.61		0.08	0.65
Total			11.35	100.00		12.24	100.00
Heptane		R1	3.35	39.09		5.81	44.02
Cumene			2.26	30.57		1.95	14.77
Ammonia			2.60	30.34		5.44	41.21
Total			8.57	100.00		13.20	100.00
Heptane		E1	0.59	6.23	E2	-	-
Cumene			0.61	6.44		-	-
Ammonia			8.27	87.33		-	-
Total			9.47	100.00		-	-
Heptane	EX3	F1	7.62	63.03	F2	7.98	63.18
Cumene			4.36	36.06		4.53	35.87
Ammonia			0.11	0.91		0.12	0.95
Total			12.09	100.00		12.63	100.00

cont..

			Vol. (cc)	Vol. %			
Heptane		R1	1.13	13.47	R2	0.62	9.44
Cumene			0.83	9.89		0.33	5.02
Ammonia			6.43	76.64		5.62	85.54
Total			8.39	100.00		6.57	100.00
Heptane		E1	1.15	16.31	E2	0.17	5.96
Cumene			1.24	17.59		0.23	8.07
Ammonia			4.66	66.10		2.45	85.97
Total			7.05	100.00		2.85	100.00
Heptane	EX4	F1	7.87	62.71	F2	5.44	63.90
Cumene			4.46	35.54		2.93	34.39
Ammonia			0.22	1.75		0.15	1.76
Total			12.55	100.00		8.52	100.00
Heptane		R1	3.80	64.52	R2	5.04	25.35
Cumene			0.71	12.05		2.81	14.14
Ammonia			1.38	23.43		12.03	6.51
Total			5.89	100.00		19.88	100.00
Heptane		E1	1.30	13.98	E2	1.6	10.58
Cumene			0.84	9.03		0.97	6.42
Ammonia			7.16	76.99		12.55	83.00
Total			9.30	100.00		15.12	100.00
Heptane	EX5	F1	7.10	47.05	F2	6.21	47.70
Cumene			7.74	51.29		6.63	50.92
Ammonia			0.25	1.66		0.18	1.38
Total			15.09	100.00		13.02	100.00
Heptane		R1	6.26	55.01	R2	1.17	9.30
Cumene			3.13	27.50		1.66	13.20
Ammonia			1.99	17.49		9.75	77.50
Total			11.38	100.00		12.58	100.00
Heptane		E1	1.42	9.94		-	-
Cumene			2.01	14.07		-	-
Ammonia			10.86	75.99		-	-
Total			14.29	100.00		-	-

Appendix 10A

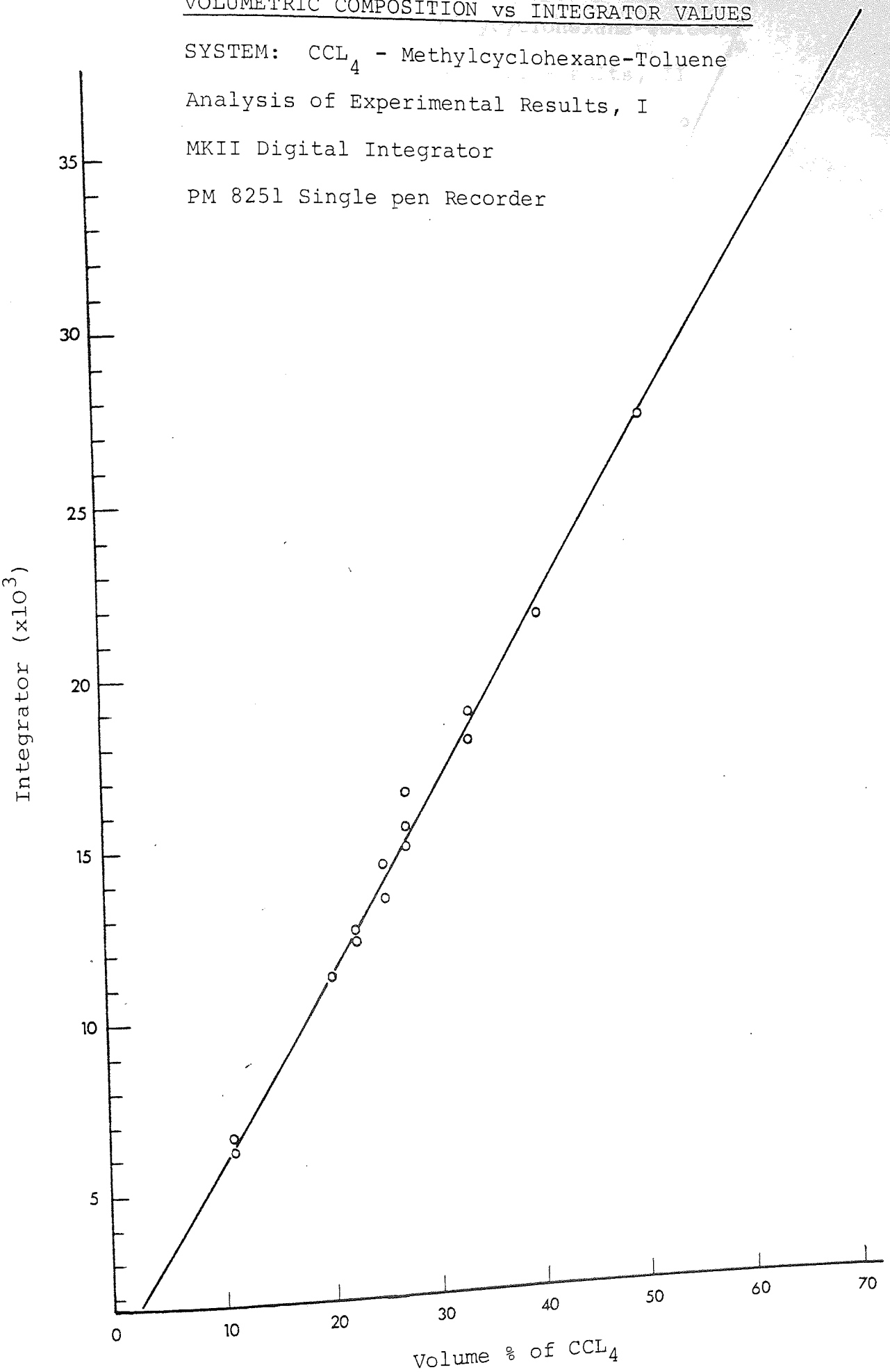
VOLUMETRIC COMPOSITION vs INTEGRATOR VALUES

SYSTEM: CCL_4 - Methylcyclohexane-Toluene

Analysis of Experimental Results, I

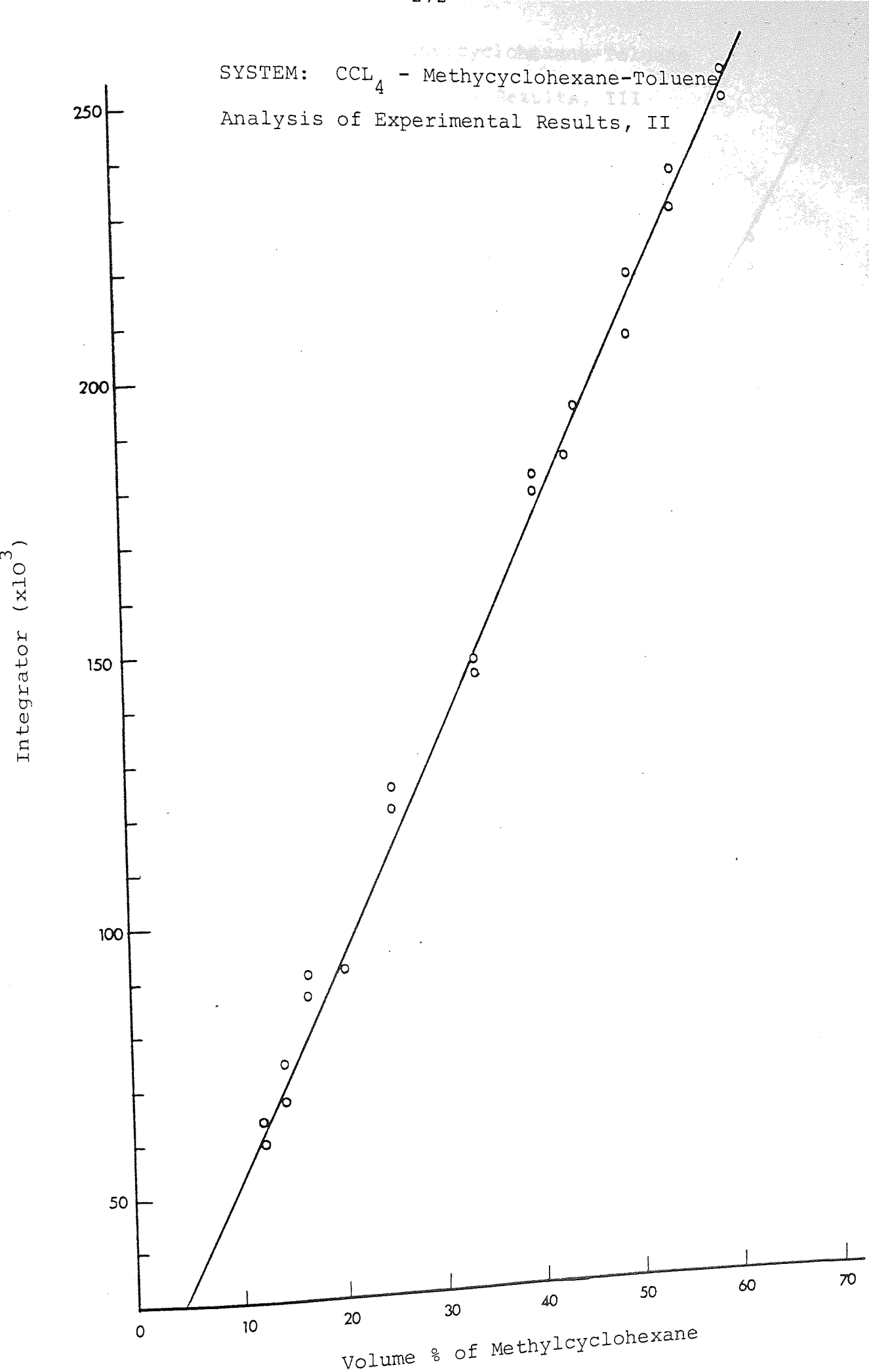
MKII Digital Integrator

PM 8251 Single pen Recorder



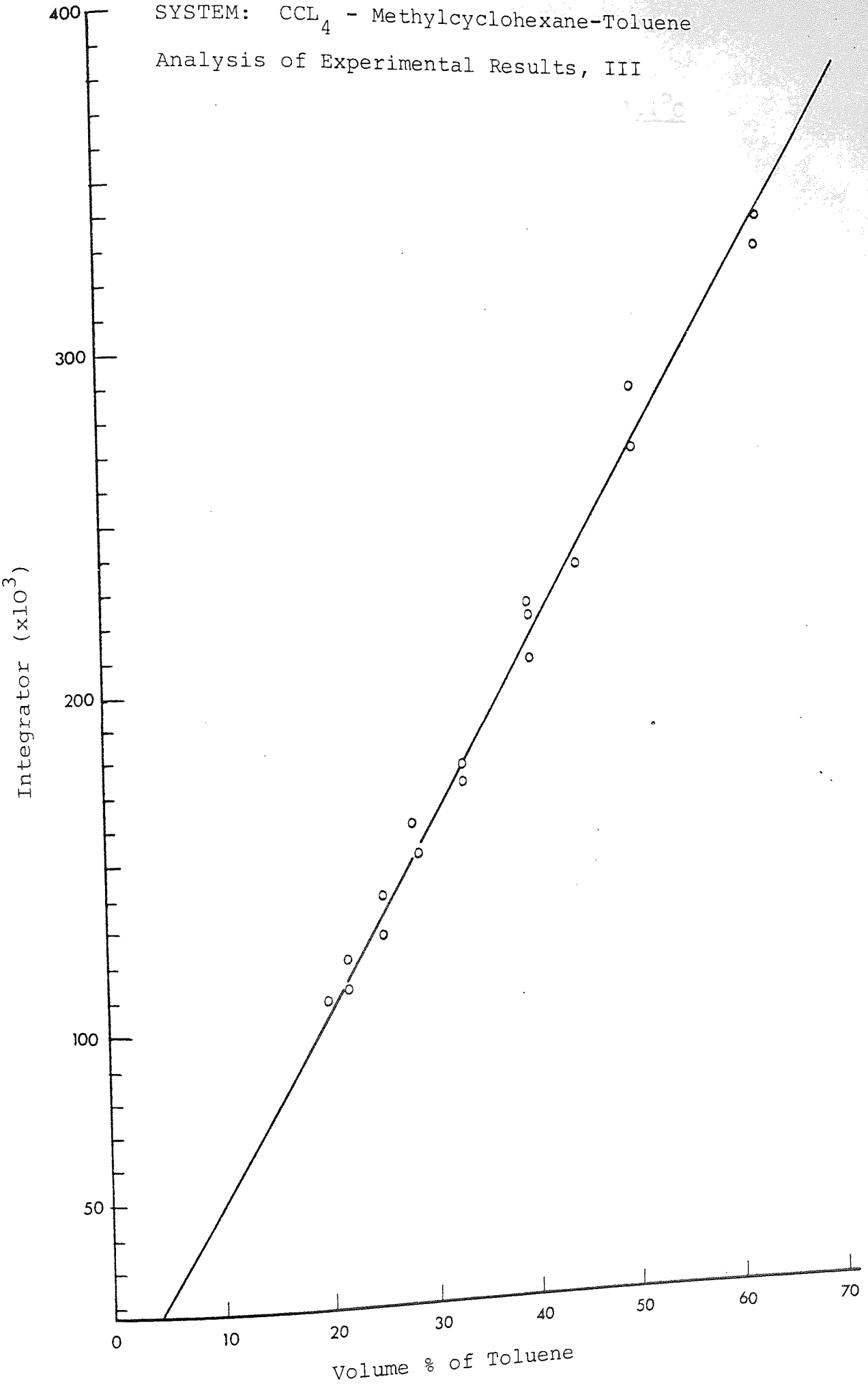
SYSTEM: CCL_4 - Methycyclohexane-Toluene

Analysis of Experimental Results, II



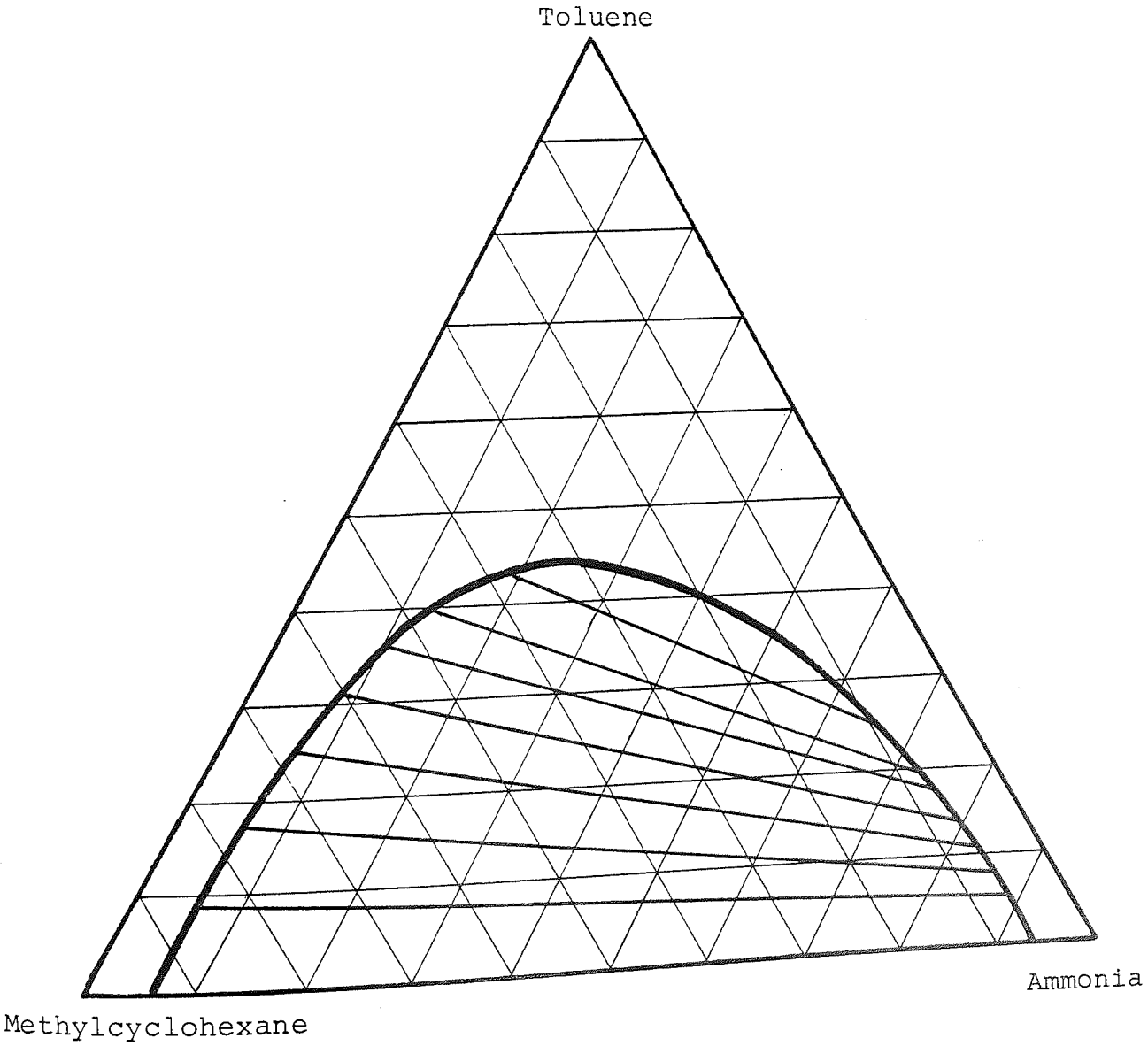
SYSTEM: CCL_4 - Methylcyclohexane-Toluene

Analysis of Experimental Results, III



Appendix 10B

EQUILIBRIUM CURVE AND TIE LINE DATA AT 21.1°C



Appendix 10C

HYDROCARBONS ANALYSIS BY F.I.D. FOR SYSTEM:

METHYLCYCLOHEXANE-TOLUENE-AMMONIA

Experiment 1
Rotor speed = 300 r.p.m., Solvent/Feed (vol) = 1/1
(MCH = methylcyclohexane)

	Integrator	Vol. %	Corrected Vol. %	Vol. (cc)
F1				
CCl_4	27096	49.25	46.68	10.00
MCH	197220	45.25	42.89	9.19
Toluene	55119	11.00	10.43	2.23
Total		105.50	100.00	21.42
F2				
CCl_4	8612	15.00	13.51	10.00
MCH	328883	77.25	69.60	51.52
Toluene	99207	18.75	16.89	12.50
Total		111.00	100.00	74.02
R1				
CCl_4	22509	41.00	40.00	10.00
MCH	235116	54.50	53.17	13.29
Toluene	34522	7.00	6.83	1.71
Total		102.50	100.00	25.00
R2				
CCl_4	27899	50.75	51.39	10.00
MCH	183105	41.5	42.03	8.18
Toluene	30087	6.5	6.58	1.28
Total		98.75	100.00	19.46
E1				
CCl_4	49136	90.00	85.92	10.00
MCH	40011	6.75	6.44	0.75
Toluene	38220	8.00	7.64	0.89
Total		104.75	100.00	11.64
E2				
CCl_4	46295	84.75	83.09	10.00
MCH	43011	7.50	7.35	0.89
Toluene	48721	9.75	9.56	1.15
Total		102.00	100.00	12.04

Experiment 2
Rotor speed = 300 r.p.m. Solvent/Feed = 1/1

	Integrator	Vol. %	Corrected Vol. %	Vol. (cc)
F1				
CCl_4	33850	61.75	57.99	10.00
MCH	129337	27.00	25.35	4.38
Toluene	93108	17.75	16.67	2.87
Total		106.50	100.00	17.25
F2				
CCl_4	24612	44.75	42.52	10.00
MCH	160023	36.25	34.44	8.10
Toluene	130116	24.25	23.04	5.42
Total		105.25	100.00	23.52
R1				
CCl_4	23011	41.75	47.04	10.00
MCH	178752	40.75	45.92	9.76
Toluene	28550	6.25	7.04	1.50
Total		88.75	100.00	21.26
R2				
CCl_4	34679	55.50	53.24	10.00
MCH	180072	41.25	39.57	7.43
Toluene	35620	7.50	7.19	1.35
Total		104.25	100.00	18.78
E1				
CCl_4	41688	76.50	73.91	10.00
MCH	47092	8.50	8.21	1.11
Toluene	96610	18.50	17.88	2.42
Total		103.50	100.00	13.53
E2				
CCl_4	45582	83.75	85.24	10.00
MCH	28509	4.00	4.07	0.48
Toluene	50833	10.50	10.69	1.25
Total		98.25	100.00	11.73

Experiment 3
Rotor speed = 300 r.p.m. Solvent/Feed = 1/5

	Integrator	Vol. %	Corrected Vol. %	Vol. (cc.)
F1				
CCl_4	36676	66.50	58.59	10.00
MCH	157961	30.75	27.09	4.63
Toluene	84714	16.25	14.23	2.44
Total		113.50	100.00	17.07
F2				
CCl_4	41337	75.50	64.26	10.00
MCH	127442	28.25	24.04	3.74
Toluene	71755	13.75	11.70	1.82
Total		117.50	100.00	15.56
R1				
CCl_4	27920	50.75	47.18	10.00
MCH	164733	37.25	34.63	7.34
Toluene	96211	18.50	17.19	3.65
Total		106.50	100.00	21.19
R2				
CCl_4	23366	42.25	39.76	10.00
MCH	213509	49.50	46.59	11.72
Toluene	73154	14.50	13.65	3.43
Total		106.25	100.00	25.15
E1				
CCl_4	46656	85.75	84.07	10.00
MCH	32335	5.00	4.90	0.58
Toluene	57211	11.25	11.03	1.31
Total		102.00	100.00	11.89
E2				
CCl_4	47999	88.25	81.90	10.00
MCH	34526	5.50	5.11	0.62
Toluene	72110	14.00	12.99	1.59
Total		107.75	100.00	12.21

Experiment 4
Rotor speed = 300 r.p.m. Solvent/Feed = 1/2

	Integrator	Vol. %	Corrected Vol. %	Vol. (cc.)
F1				
CCl_4	16025	38.75	27.78	10.00
MCH	198920	45.75	44.20	15.91
Toluene	155917	29.00	28.02	10.09
Total		103.50	100.00	36.00
F2				
CCl_4	20039	36.25	36.71	10.00
MCH	166521	37.75	38.23	10.41
Toluene	133170	24.75	25.06	6.83
Total		98.75	100.00	27.24
R1				
CCl_4	24916	45.25	43.30	10.00
MCH	20201	46.50	44.50	10.28
Toluene	65337	12.75	12.20	2.82
Total		104.50	100.00	23.10
R2				
CCl_4	25236	45.75	42.86	10.00
MCH	209311	48.25	45.20	10.55
Toluene	59220	12.75	11.94	2.78
Total		106.75	100.00	23.33
E1				
CCl_4	49074	90.25	80.94	10.00
MCH	41120	7.00	6.28	0.77
Toluene	72975	14.25	12.78	1.58
Total		111.50	100.00	12.35
E2				
CCl_4	44239	81.25	79.27	10.00
MCH	38099	6.25	6.10	0.77
Toluene	78116	15.00	14.63	1.85
Total		102.25	100.00	12.62

AMMONIA ANALYSIS BY TITRATION FOR SYSTEM:

METHYCYCLOHEXANE-TOLUENE-AMMONIA

For all raffinate and extract samples 500 cc. 1.N. H_2SO_4 solution was used.

		Vol. 0.5 N NaOH used to titrate 25cc. 1.N. H_2SO_4	NH_3 amount (cc.)
EX1	R1	47.1	0.82
	R2	47.8	0.62
	E1	2.3	13.29
	E2	8.5	11.56
EX2	R1	48.2	0.51
	R2	48.0	0.57
	E1	13.0	10.31
	E2	28.1	6.10
EX3	R1	45.6	1.24
	R2	41.5	2.38
	E1	17.6	9.03
	E2	3.0	13.09
EX4	R1	47.6	0.71
	R2	45.4	1.29
	E1	19.1	8.61
	E2	5.1	12.51

OVERALL EXPERIMENTAL RESULTS, SYSTEM:

METHYLCYCLOHEXANE-TOLUENE-AMMONIA

			Vol.(cc)	Vol. %		Vol.(cc)	Vol. %
MCH	EX1	F1	9.19	80.47	F2	51.52	80.48
Toluene			2.23	19.53		12.50	19.52
Ammonia			-	-		-	-
Total			11.42	100.00		74.02	100.00
MCH		R1	13.29	84.01	R2	8.18	81.15
Toluene			1.71	10.81		1.28	12.70
Ammonia			0.82	5.18		0.62	6.15
Total			15.82	100.00		10.08	100.00
MCH		E1	0.75	5.02	E2	0.89	6.54
Toluene			0.89	5.96		1.15	8.45
Ammonia			13.29	89.02		11.56	85.00
Total				100.00		13.60	100.00
MCH	EX2	F1	4.38	60.41	F2	8.10	59.91
Toluene			2.87	39.59		5.42	40.09
Ammonia			-	-		-	-
Total			7.25	100.00		13.12	100.00
MCH		R1	9.76	82.92	R2	7.43	79.47
Toluene			1.50	12.74		1.35	14.44
Ammonia			0.51	4.34		0.57	6.09
Total			11.77	100.00		9.35	100.00
MCH		E1	1.11	8.02	E2	0.48	6.13
Toluene			2.42	17.49		1.25	15.96
Ammonia			10.31	74.49		6.10	77.91
Total			13.84	100.00		7.83	100.00
MCH	EX3	F1	4.63	65.49	F2	3.74	67.27
Toluene			2.44	34.51		1.82	32.73
Ammonia			-	-		-	-
Total			7.07	100.00		5.56	100.00

			Vol.(cc)	Vol. %		Vol.(cc)	Vol. %
MCH		R1	7.34	60.02	R2	11.72	66.86
Toluene			3.65	29.84		3.43	19.57
Ammonia			1.24	10.14		2.38	13.57
Total			12.23	100.00		17.53	100.00
MCH		E1	0.58	5.31	E2	0.62	4.05
Toluene			1.31	12.00		1.59	10.39
Ammonia			9.03	82.69		13.09	85.56
Total			10.92	100.00		15.30	100.00
MCH	EX4	F1	15.91	61.19	F2	10.41	60.38
Toluene			10.09	38.81		6.83	39.62
Ammonia			-	-		-	-
Total			26.00	100.00		17.24	100.00
MCH		R1	10.28	74.44	R2	10.55	72.16
Toluene			2.82	20.42		2.78	19.02
Ammonia			0.71	5.14		1.29	8.82
Total			13.81	100.00		14.62	100.00
MCH		E1	0.77	7.03	E2	0.77	5.09
Toluene			1.58	14.42		1.85	12.23
Ammonia			8.61	78.55		12.51	82.68
Total			10.96	100.00		15.13	100.00

Appendix 11

CALCULATION OF MASS TRANSFER RATE

Experiment 2 - Toluene-Methylcyclohexane-Ammonia

System Properties:

D_k = 5cm. D_i = 2.9cm.

D_s = 3.7cm. H_c = 2.1cm.

ρ_c = 0.803 ρ_d = 0.611

$\mu_c = 1.817 \times 10^{-2}$ $\mu_d = 0.31 \times 10^{-2}$

σ_c = 30.2 dyn/cm. σ_d = 21.35 dyn/cm.

Q_c = 0.25 l/min. Q_d = 0.25 l/min.

(Symbols are defined in nomenclature).

To evaluate the mass transfer rate involves use of Equation 2.1.; $N = k A \Delta c$

1. Calculation of mass transfer area

prediction of drop diameter

a) from Kolomogorof 's equation (4.29):

$$r_{sd} = \sqrt{2} \left(\frac{\gamma}{k_f \rho_d}\right)^{3/5} \left(\frac{L^{2/5}}{V^{6/5}}\right)$$

$d = 0.7 \times d_{sd}$ (4.32)

$d = 0.223$ cm.

b) Misek's correlation:

$$d = 0.38 \sqrt{\frac{\gamma}{\Delta \rho g}}$$

$d = 0.82$cm.

Drop Reynolds Number

$$Re = \frac{d_o V_k \rho_c}{\mu_c}$$

$Re = 69.804$

$Re = 25.67$

Characteristic velocity, V_k, from;

$$\frac{\bar{V}_N \mu_c}{\gamma} = 0.012 \left(\frac{\Delta\rho}{\rho_c}\right) \left(\frac{g}{D_i N^2}\right) \left(\frac{D_s}{D_i}\right)^{2.3} \left(\frac{H_c}{D_i}\right)^{2.6} \left(\frac{D_i}{D_k}\right)^{2.6} \qquad (4.7)$$

$$\bar{V}_N = 7.083 \text{ cm/sec.}$$

Drop terminal velocity:

$$V_t = \frac{\bar{V}_N}{C_R} \qquad C_R = \left(\frac{D_s}{D_k}\right)^2 = 0.5476$$

$$V_t = 12.93 \text{ cm/sec.}$$

Continuous, Dispersed Phase velocities:

$$V_c = \frac{Q_c}{a} \qquad V_c = 0.2122 \text{ cm/sec.}$$

$$V_d = \frac{Q_d}{a} \qquad V_d = 0.2122 \text{ cm/sec.}$$

Hold-up, X, Calculation from;

$$\frac{V_d}{X} + \frac{V_c}{1-X} = \bar{V}_N (1-X) \exp\left(\frac{Z}{\gamma} - 4.1\right) X \qquad (4.8)$$

$$Z = 1.59 \times 10^{-2} \left(\frac{D}{u_c} \left(\frac{\gamma}{\rho_c d_o}\right)^{\frac{1}{2}}\right)^{\frac{1}{2}} \qquad (4.9)$$

related to drop Reynolds Number

$Z = 0.6266$

$= 0.98$

$$\frac{V_d}{X} + \frac{V_c}{1-X} = \bar{V}_N (1-X) \exp(-3.461X)$$

$X = 0.441$

$Z = 0.8046$

$\alpha = 0.86$

$$\frac{V_d}{X} + \frac{V_c}{1-X} = \bar{V}_N (1-X) \exp(-3.164X)$$

$X = 0.47$

Dispersed phase volume in R.D.C.

V = X column,

Number of drops

$$n = \frac{V}{\frac{4}{3} \pi r^3}$$

Mass Transfer Area:

$$A = n \pi r^2$$

$V = 831.34\ cm^3$	$V = 886.02\ cm^2$
$n = 143174$	$n = 3069045$
$A = 22368.1\ cm^2$	$A = 64830.7\ cm^2$

Distribution Coefficient from Figure A 11:

$m = 2.3$

Mass Transfer Coefficient

Mass Transfer Coefficient for the Continuous Phase

Diffusivity, D;

$$= \frac{7.4 \times 10^{-8} (\Phi M_B)^{0.5} T}{\mu V_A^{0.6}}$$

$$= 0.3626 \times 10^{-4} \frac{cm^2}{sec}$$

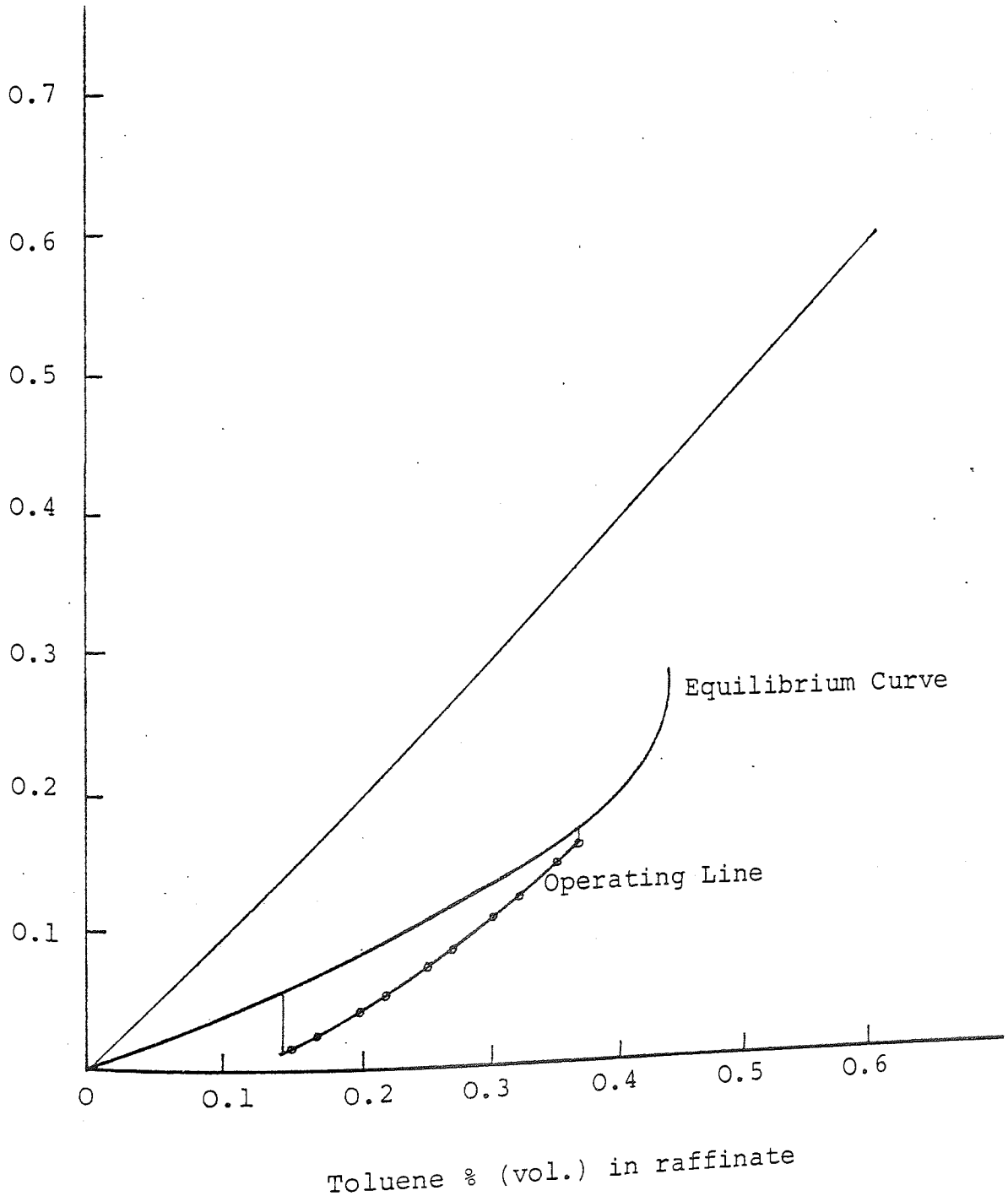
$k_c = \sqrt{\frac{4\bar{V}_N}{d_o}}$	$k_c = 0.001\ \bar{V}_N(1-X)$
$k_c = 0.06787$ cm/sec.	$k_c = 0.00375$ cm./sec.

Mass Transfer Coefficient for the Dispersed Phase

$k_d \quad 17.9 \frac{D}{d_o}$	$k_d = \frac{2\pi^2 D}{3d_o}$

Figure A11

DISTRIBUTION DIAGRAM FOR CONCENTRATION DRIVING FORCE



k_d = 0.00291 cm/sec. | k_d = 0.0010699 cm/sec.

Overall mass transfer coefficient

$$\frac{1}{K} = \frac{1}{k_c} + \frac{m}{k_d}$$

K = 0.001242 cm/sec. | K = 0.000663 cm/sec.

Mean driving force; Δc;

from distribution coordinates;

applying Simpson's rule

$$\Delta c = \frac{1}{18} (\Delta y_1 + 4\Delta y_2 + 2\Delta y_3 + 4\Delta y_4 + 2\Delta y_5 + 4\Delta y_6 + \Delta y_7)$$

Δy_1 = 0.0725 Δy_4 = 0.037 Δy_7 = 0.012

Δy_2 = 0.05 Δy_5 = 0.03

Δy_3 = 0.047 Δy_6 = 0.021

Δc = 0.03725

N = Δc A K

= 1.0155 cm^3/sec.

= 60.58 cm^3/min. | N = 1.59 cm^3/sec.

= 95.42 cm^3/min.

Feed contains 39.5% Toluene, i.e. 0.395 x 250 = 98.75 $\frac{cm^3}{min.}$

Raffinate contains 14.5% Toluene

Extract contains 17.5% Toluene

Therefore:

E = 346.18 cm^3/sec. | E = 545.0

R = 263.1 cm^3/sec. | R = 22.89

F = 250 cm^3

S = 250 $\frac{cm^3}{min.}$

For circulating drops

E + R = 609 $\frac{cm^3}{min}$

For stagnant drops

E + R = 567.9 $\frac{cm^3}{min.}$

NOMENCLATURE

A,a	Interfacial area
a_o	Initial radius or half axis length
a_p	Amplitude
ΔC, Δc	Concentration driving force
C,c	Solute concentration
C_1, C_2	Constants
D, D_D	Diffusivity
D_E	Equivalent diffusivity
D,D_k	Column diameter
D_s	Stator ring diameter
D_i	Disc diameter
d	Drop diameter
d_{32}	Sauter mean drop diameter
E	Extract phase volumetric flowrate
E	Eddy diffusivity
E	Energy
F	Harkin and Brown correction factor
F	Feed volumetric flowrate
f	Mean actual interstage mixing per unit area of stator opening.
H,H_c	Compartment height
HTU	Height of transfer unit
H_{eff}	Effective column height
i	ith stage
K_1, K_2	Constants
K	Overall mass transfer coefficient
k	Individual mass transfer coefficient
k_{df}	Mass transfer coefficient for the forming drops

L	Macroscale of turbulence or flowrate
M	Velocity exponent
m	Distribution coefficient
n	Compartment number
N	Mass transfer rate
N	Revolutions per second
N_{Pe}	Peclet number
NTU	Number of transfer units
P	Energy input
Pe	Peclet number
Q	Volumetric flowrate
R	Raffinate volumetric flowrate
R	Disc diameter
Re	Reynolds number
S	Solvent volumetric flowrate
S	Stator diameter
Sc	Schmidt number
Sh	Sherwood number
t	Time
V	Velocity, resultant sheet velocity
$\bar{V}_N$	Characteristic velocity
V_S	Slip velocity
V_t	Terminal velocity
W	Axial velocity component
X,x	Dispersed phase hold-up
Z	Coalescence coefficient

Greek Letters

α	Velocity component
β	Selectivity

γ	Interfacial tension
μ	Viscosity
ξ	Dimensionless distance from wall
Φ	Association factor for the solvent
$\bar{\Phi}$	Hold-up
π	3.14
ρ	Density
σ	Surface tension
ψ	A function

Subscripts

C,d	Continuous, coalescence
D,d	Dispersed
E,e	Extract, efficiency
F	Formation
f	Flooding
i	ith stage
m	maximum
p	Plug flow condition
R	Raffinate
s	Stagnant drop
sd	Stable drop
vs	Mean

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